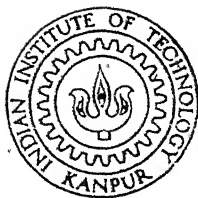


✓ COMPLEXING BEHAVIOURS
OF
2,4-DITHIOURACIL AND 3,4,5-PYRIDAZINE TRITHIOL

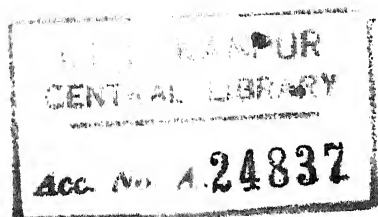
A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

BY
J. S. DWIVEDI



to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
DECEMBER, 1972



2 JUL 1973

D E D I C A T E D

T O

M Y P A R E N T S

CONTENTS

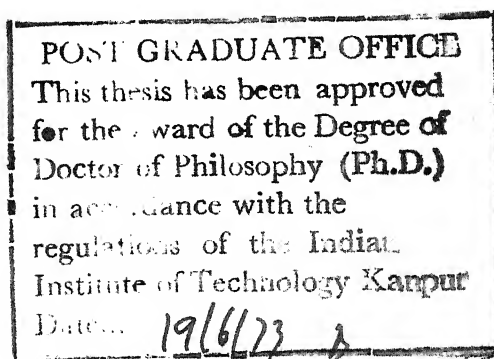
	Page
STATEMENT	i
CERTIFICATE I	ii
CERTIFICATE II	iii
ACKNOWLEDGEMENTS	iv
PREFACE	v
CHAPTER I Introduction	1
CHAPTER II Chelating Behaviour of 2,4-Dithiouracil-I (Co(II), Ni(II), Cu(II), Cd(II), Pb(II), Ag(I), Tl(I) and Au(II))	55
CHAPTER III Chelating Behaviour of 2,4-Dithiouracil-II (Rh(III), Ru(III), Pd(II), Pd(IV), Pt(II) and Pt(IV))	83
CHAPTER IV Chelating Behaviour of 2,4-Dithiouracil-III (Pd(0), Rh(I), Rh(II) and Ru(II))	99
CHAPTER V Chelating Behaviour of 3,4,5-Pyridazine Trithiol-I (Co(II), Cu(II), Ni(II), Fe(III) and Cr(III))	120
CHAPTER VI Chelating Behaviour of 3,4,5-Pyridazine Trithiol-II (Pd(0), Pd(II), Rh(I), Rh(II), Rh(III), Ru(II), Ru(III), Pt(II) and Pt(IV)).	139
CHAPTER VII Chelating Behaviour of 3,4,5-Pyridazine Trithiol-II (Au(III), Pb(II), Cd(II), Ag(I), Tl(I) and Hg(II))	166
CHAPTER VIII Summary	183
LIST OF PUBLICATIONS	vii
VITAE	viii

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology Kanpur, India, under the supervision of Professor U.C. Agarwala.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

J.S. Dwivedi
(J.S. DWIVEDI)



DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

CERTIFICATE I

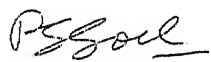
This is to certify that Mr. J.S. Dwivedi has satisfactorily completed all the courses required for the Ph.D. degree programme.

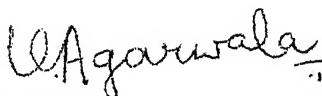
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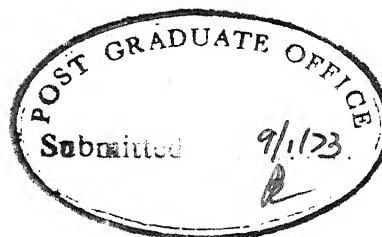
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Chm 521 Chemical Binding
Chm 523 Chemical Thermodynamics
Chm 524 Modern Physical Methods in Chemistry
Chm 534 Electronics for Chemist
Chm 541 Advanced Inorganic Chemistry I
Chm 542 Advanced Inorganic Chemistry II
Chm 622 Chemical Kinetics
Chm 642 Applications of Nuclear Chemistry
Chm 800 Gen. Seminar
Chm 801 Special Graduate Seminars
Chm 900 Post-Graduate Research

Mr. J.S. Dwivedi successfully completed his Ph.D.

Qualifying Examination in September ¹⁹⁶⁹~~1968~~.


(P.S. GOEL)
Head,
Department of Chemistry


(U.C. AGARWALA)
Convener
Departmental Post-Graduate Committee



iii

CERTIFICATE II

Certified that the work contained in this thesis entitled, "COMPLEXING BEHAVIOURS OF 2,4-DITHIOURACIL AND 3,4,5-PYRIDAZINE TRITHIOL", has been carried out by Mr. J.S. Dwivedi under my supervision and the same has not been submitted elsewhere for a degree.

U.C. Agarwala

U.C. Agarwala
Thesis Supervisor
Assistant Professor
Department of Chemistry

ACKNOWLEDGEMENTS

It is with great pleasure that I place on record my deep sense of gratitude to Professor U.C. Agarwala for suggesting the problem and encouraging me throughout these investigations with his invaluable guidance.

I wish to extend my sincere thanks to Professor C.N.R. Rao, Department of Chemistry and Professor R. Prasad, Department of Humanities for their encouragement and help without which work would have been difficult to complete.

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Valuable assistance provided by Mr. R.D. Singh for typing the thesis, Mr. A.H. Siddiqui for microanalyses of all the samples and Mr. R.K. Bajpai for tracing the figures is duly acknowledged.

Finally, I wish to express my sincere thanks to the authorities of the Indian Institute of Technology, Kanpur, for providing me the scholarship and necessary facilities.

Kanpur
December, 1972

J.S. Dwivedi

PREFACE

There has been considerable interest in the last twenty years in the study of the complexes with ligands having sulphur as donor atom. However, a coherent picture of the donor acceptor relationship between sulphur and the metal ions is not yet clear. It will, therefore, be interesting to study the complexes of sulphur containing ligand in order to seek a correlation between the different physico-chemical properties of the various metal complexes of such ligands. In the present work such a correlation is attempted. The ligands employed for complexation are (i) 2,4-dithiouracil & (ii) 3,4,5-pyridazine trithiol. The metal ions used as central cations are: Pd(0), Pd(II), Pd(IV), Pt(II), Pt(IV), Rh(I), Rh(II), Rh(III), Ru(II), Ru(III), Co(II), Ni(II), Cu(II), Cr(III), Fe(III), Pb(II), Cd(II), Au(III), Ag(I) and Tl(I).

The complexes of the above mentioned cations with the ligands have been characterized by elemental analyses, spectroscopic (visible and i.r.) and magnetic susceptibility data. Their probable structures have been elucidated on the basis of the above studies.

In Section A of the thesis, the methods of preparation of the various metal complexes with 2,4-dithiouracil are given. It has been suggested that its complexes with Ru(II), Rh(III), Pd(IV), Pt(IV), Ni(with pyridine) are octahedral, Cu(II) and Ni(without pyridine), distorted octahedral, Ru(III), octahedral with metal-metal interaction, Pd(0), Cd(II), Pb(II), Tl(I) and Ag(I), tetrahedral and those of

Rh(I), Rh(II), Pt(II), Pd(II) and Au(III), square planar. It has also been found that the ligand is behaving as tetradentate in Cd(II), Ni(II), Pb(II) and Ru(II), tridentate in Cu(II), bidentate in Co(II), Tl(I), Rh(III), Ru(III), Pd(II), Pd(IV), Pt(II), Pt(IV), and Rh(II) and monodentate in Ag(I), Pd(0) and Rh(I).

In Section E of the thesis, the methods of preparation of the various metal complexes with 3,4,5-pyridazine trithiol are given. This ligand, apart from having H-N-C-S group also contains 1,2-dithiolene group. It has been suggested that its complexes with Ru(II), Rh(III), Pt(IV), Rh(II), Ru(III) and Cu(II) are octahedral, Ni(II), distorted octahedral, Pd(0), Cd(II), Pb(II), Hg(II) and Tl(I), tetrahedral, Pt(II), Pd(II), Au(III), square-planar and those of Fe(III) and Co(II) probably pyramidal or square-planar. The ligand behaves in these complexes as mono-, bi-, tri-, tetra- or pentadentate.

CHAPTER I

INTRODUCTION

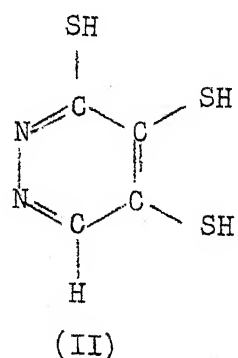
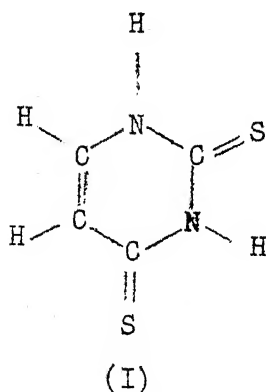
OBJECT AND SCOPE OF WORK

The available data on metal-sulphur bond are not sufficient to provide a fairly coherent picture of the donor acceptor relationship between sulphur and transition metal ions. The nature of the ligand as well as that of the central atom plays an important role in deciding the position of the metal-sulphur stretching frequency in complexes.¹⁻⁵ In the last few years, a considerable interest has been taken to study the electronic structure of square-planar complexes. This interest is partly due to the fact that relative energies of the d-orbitals in square planar complexes are not known with certainty and partly because the principal factors involved in the stabilization of the square planar geometry of the transition

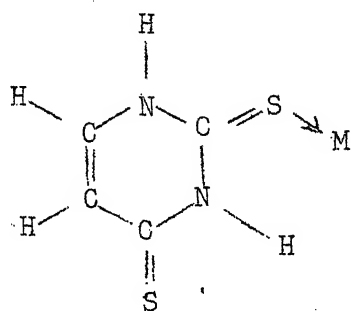
metal complexes have not yet been completely resolved. Gray, et al.⁶⁻⁸ have shown that these factors may be (a) involvement of the metal out of plane orbitals (d_{xz} , d_{yz} and p_z) in an extensive π -orbital network spanning the entire complex and thus allowing as much delocalization of the charge as possible, (b) the nature of the metal-ligand bond (predominating σ or π -character in the bond). They have reasoned that the way to stabilize the planar geometry is to involve the metal p_z valence orbital in such an extensive π -orbital network that the total π -stabilization would overcome the extra stability gained when p_z orbital is used to form extra σ -bonds with axial groups.

For most simple ligands⁹ the metal-donor atom stretching frequencies are expected in the range 250-600 cm^{-1} . The framework bending vibrations cover a wider frequency range, being as high as 800 cm^{-1} and as low as 100 cm^{-1} . It is clear then that in order to derive detailed information about the potential forces within the framework of a complex, spectra must be measured to low energy. The replacement of ligand or metal ion in a complex is generally accompanied by (a) an increase in point mass and equilibrium separation may be expected to decrease the corresponding frequencies and in case the ligand replacement involves a change in bond-type, it will have a more pronounced effect leading to an increase in frequency as the bond order increases, (b) a variation in bonding capacity of the central metal ion in complexes M_iL , where M_i are the various metal ions and L is a particular ligand.

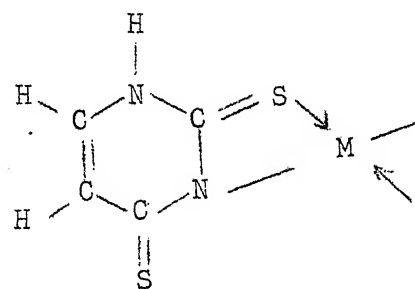
It will, therefore, be interesting to seek these types of correlations using various types of sulphur containing ligands and different metal ions, as the central atoms in the complexes. Even more interesting will be the study of those complexes, where there is an extensive delocalization of charges. The present work is an attempt in the direction of seeking such a correlation between the different physicochemical properties of the complexes with ligands having thiocarbonyl or thiol sulphur and nitrogen as potential donors. Moreover, the ligands chosen in this study are such that the charge is delocalized between thiol sulphur and thiol sulphur and thione sulphur and nitrogen atoms. This may lead in a semi-quantitative way to a better understanding of (a) the donor property of sulphur in general, (b) nature of metal-sulphur link, (c) position of the ligands, having sulphur and nitrogen or sulphur alone as donor sites, in the spectrochemical and nephelauxetic series, (d) stereochemistry and coordination number of the transition metal ions and finally, (e) the stability of square-planar complexes with ligands having declocalized system. The ligands whose complexing properties have been studied in this thesis are 2,4-dithiouracil(I)¹⁰ and 3,4,5-pyridazine trithiol(II).¹¹



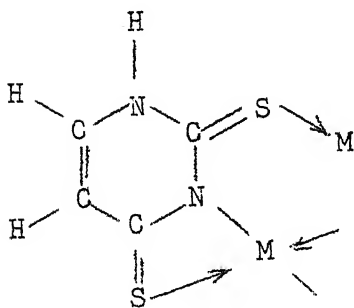
2,4-Dithiouracil(I), which is assumed in thione form (reason cited elsewhere¹²) has two thiocarbonyl sulphur and two nitrogen atoms as potential donors. Thus, it can act as mono-, or bi-, or tri-, or tetradentate ligand as shown by the structures III, IV, V and VI.



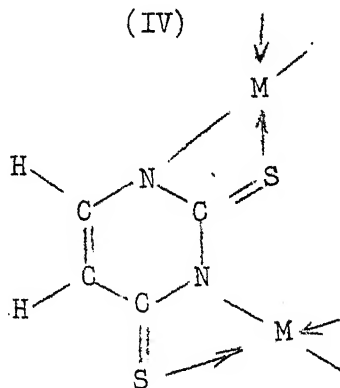
(III)



(IV)



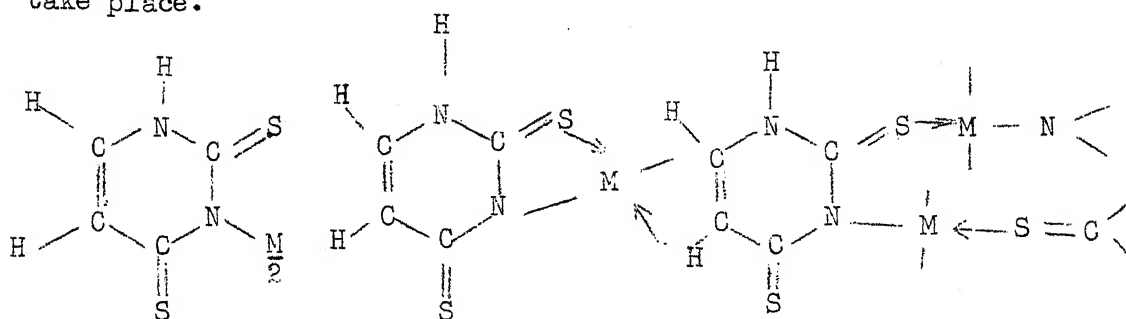
(V)



(VI)

Moreover when the ligand is behaving as bidentate, the metal ion can form either a simple salt VII by linking with one of the nitrogen atoms or an inner complex VIII or a polymer IX by forming bonds with nitrogen and sulphur atoms. In the structures VII, VIII and IX, the coordinations utilizing 2,3-positions have been shown.

However, the coordination utilizing 1,2- or 3,4-positions may also take place.

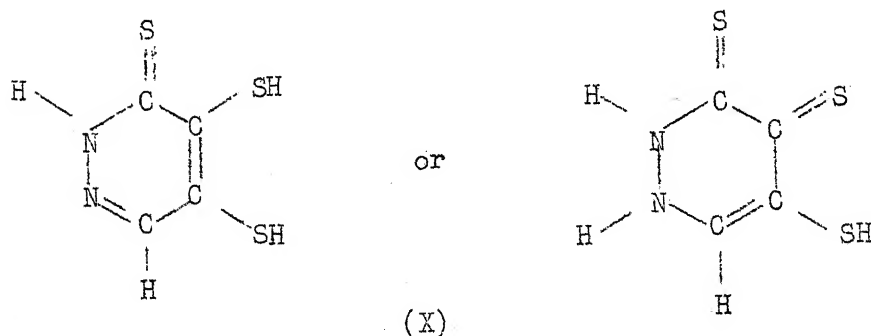


(VII)

(VIII)

(IX)

Similarly, 3,4,5-pyridazine trithiol(II) has two nitrogen and three sulphur atoms as potential donors and it can act as mono-, or bi-, or tri-, or tetra-, or pentadentate depending upon the mode of linkage with the metal ion. Also the ligand can either act in the form of thione-thiol (X) or thiol (II) as shown below:



(X)

It has been well established that some of the transition metal ions have a greater affinity for sulphur as compared to other

atoms (cf. class 'a' and 'b' type metal¹³ or hard and soft acids)¹⁴⁻¹⁶ which could tentatively be explained in the light of π -bond formation,*

* Though there have been some doubts regarding this explanation.

the symmetry of the ligand field and the hybridization involved. Thus, the metal ions used for complexation in these studies are class 'b' metal, like rhodium, ruthenium and platinum.

In the first and second parts of the thesis the preparation of the complexes of Rh(I), Rh(II), Rh(III), Ru(II), Ru(III), Pd(0), Pd(II), Pd(IV), Pt(II), Pt(IV), Au(III), Co(II), Cu(II), Ni(II), Fe(III), Cr(III), Tl(I), Ag(I), Pb(II), Cd(II) and Hg(II) have been reported. The stoichiometries, bond types and the oxidation states of the central metal ions in these complexes (given in Table I) have been studied by the infrared and visible spectra, and the magnetic susceptibility measurements. The stoichiometries and spatial arrangements of these complexes have been given in Table I.

NATURE OF METAL SULPHUR BOND

The strength and stability of metal donor bond depends upon the nature of the metal and the donor atom of the ligand, their size, electronegativity, nature of the orbitals involved and their overlapping capacity, more specifically on their electronic structure. The ligand donor atoms may be attached with other atoms, the number and the nature of which will also influence the stability of the

Stereochemistry, Solubility and Colour of the Complexes

Ligand	No.	Complex Formula	Stereochemistry	Solubility	Colour
1. 2,4-Dithiouracil (TU, TUH)	1	$\text{Pd}(\text{TUH})_2(\text{P}\phi_3)_2$	Tetrahedral	I	Reddish orange
	2	$\text{Rh}_3(\text{TUH})_4\text{Cl}_2(\text{P}\phi_3)_2$	Square planar	I	Orange yellow
	3	$[\text{Rh}(\text{TU})_2\text{H}_2\text{O}]_2$	Octahedral with metal-metal interaction	I	Brown
	4	$\text{Ru}_2(\text{TUH})_3(\text{H}_2\text{O})_2$	Octahedral	I	Dark brown
	5	$\text{Rh}(\text{TU})_2\text{Cl}$	Octahedral	I	Brown
	6	$\text{Ru}_2(\text{TU})_5\text{Cl}$	Octahedral with metal-metal bond	I	Dark gray
	7	$\text{Pd}(\text{TU})_2$	Square-planar	I	Yellowish brown
	8	$\text{Pd}_2(\text{TU})_5\text{Cl}$	Octahedral	I	Bright orange
	9	$\text{Pt}(\text{TU})_2$	Square planar	I	Yellow
	10	$\text{Pt}(\text{TU})_2\text{Cl}_2$	Octahedral	I	Yellow
	11	$\text{Co}_4(\text{TU})_9(\text{H}_2\text{O})_2$	Square-pyramidal	I	Brown
	12	$\text{Ni}(\text{TU})\text{Py}_2$	Octahedral	I	Greenish blue
	13	$\text{Cu}(\text{TU})_2$	Distorted Octahedral	I	Yellow
	14	$\text{Ni}(\text{TU})_2(\text{H}_2\text{O})_4$	Distorted Octahedral	I	Yellow
	15	$\text{Cd}(\text{TU})$	Tetrahedral	I	Cream-colour
	16	$\text{Pb}(\text{TU})$	Tetrahedral	I	Light yellow

Table I (continued)

Ligand	No.	Complex Formula	Stereochemistry	Solubility	Colour
2. 3,4-Pyridazine-trithiol (TH ₃)	17	Ag ₂ (TU)	Linear	I	Yellow
	18	Au ₂ (TU) ₃	Square-planar	I	Yellow
	19	Tl(TU)(H ₂ O) ₂	Tetrahedral	I	Bright yellow
	20	Pd(TH ₂)Pφ ₃	Tetrahedral	I	Buff colour
	21	Pd ₂ (TH) ₂ (TH ₃)	Square-planar	I	Brown
	22	Rh(TH ₂) ₂ Cl	Square-planar	I	Brown
	23	[Rh(TH ₂) ₂ H ₂ O] ₂	Octahedral	I	Brown
	24	Rh ₂ (TH) ₃	Octahedral	I	Brown
	25	Ru ₂ (TH)(TH ₂) ₂ ·6H ₂ O	Octahedral	I	Brown
	26	Ru(TH)Cl·H ₂ O	Octahedral	I	Brown
	27	Pt ₂ (TH) ₂ (TH ₃)	Square-planar	I	Black
	28	Pt(TH) ₂	Octahedral	I	Black
	29	Co(TH ₂) ₂ ·6H ₂ O	Pyramidal or Square-planar	I	Brown
	30	Ni(TH)	Distorted Octahedral	I	Brown
	31	Cu ₅ (T) ₂ (TH) ₂ ·10H ₂ O	Distorted Octahedral with metal-metal interaction	I	Black
	32	Fe(TH ₂) ₃ ·3H ₂ O	Pyramidal or Square-planar	I	Brown
	33.	Cr(T)	-	I	Brown

Table I (continued)

Ligand	No.	Complex formula	Stereochemistry	Solubility	Colour
	34	$\text{Au}_2(\text{TH})_3$	Square-planar	I	Brown
	35	$\text{Cd}(\text{TH})$	Tetrahedral	I	Yellow
	36	$\text{Pb}_3(\text{T})_2$	Tetrahedral	I	Red
	37	$\text{Ag}_3(\text{T})$	Linear	I	Brownish yellow
	38	$\text{Tl}_3(\text{TH})(\text{TH}_2) \cdot 4\text{H}_2\text{O}$	Tetrahedral	I	Dark brown
	39	$\text{Hg}_2(\text{TH})_3$	Tetrahedral	I	Yellow

I, Insoluble in chloroform, carbon tetrachloride, benzene, tetrahydrofuran, cyclohexane, xylene, toluene, acetone, methanol, dioxane, dichloro-ethane, dichloro-methane.

M-L bond. It is very difficult to isolate the influence of the nature of the donor atom on the stability, since the donor atom must be considered in relation to the acceptor atom. However, the difference in the stabilities of bonds between $M-L_1$ and $M-L_2$, where L_1 and L_2 are different donor atoms and M, the same or similar metal atoms, can be correlated with the electronic properties of L_1 and L_2 . Thus, the nature of metal-sulphur bond can be studied under two headings: (a) study of the relative affinities of different metal atoms for sulphur, (b) study of sulphur as donor ^{atoms}/relative to other donor atoms when attached to the same or similar metal atoms.

In the extreme ionic bonds, we suppose that a metal ion M^{+n} is attached to a certain number of ligands either charged or uncharged in which the bonding energy between metal and ligand is purely electrostatic type (ion-ion, ion-dipole or dipole-dipole attraction). In extreme covalent type, the bonding is essentially of the type familiar in the covalent bonds, for example, in hydrogen molecule. However, in metal to ligand bonds, the extreme covalent type of bond cannot exist as (a) the bonded atoms are of different size, (b) they have different electronegativities, and (c) they have different polarizabilities. Thus, in most of the cases the bonds will have some polar character.

Besides σ -type of covalent bonds, in which the electron density is greatest along the internuclear axis, π -type of bonds are also formed in metal complexes either by the donation of lone pair of electrons from metal to ligand donor atoms or by the ligand

donor atoms to metal atoms. The formation of π -bond affects the bonding energy tremendously. In transition metal complexes π -bond may be either $d_{\pi} - p_{\pi}$ (e.g. in $\text{Ni}(\text{CO})_4$) or $d_{\pi} - d_{\pi}$ (e.g. in $\text{Ni}(\text{PF}_3)_4$) type. In the complexes of phosphine or arsine, the situation is not clear cut, and the general consensus seems to be against extensive π -back bonding.¹⁷⁻¹⁹

SULPHUR AS A DONOR ATOM IN RELATION TO OTHER DONOR ATOMS

The polarizabilities of the common donor atoms fall in the series $\text{F}^- < \text{O}^{2-} < \text{Cl}^- < \text{Br}^- < \text{I}^- \approx \text{S}^{2-} < \text{Se}^{2-} < \text{Te}^{2-}$ which is just the electronegativity series in the reverse order. Since the increased polarizability of an atom means the increased tendency to form a covalent bond, the metal sulphur bond should have more of partial covalent character than that of M-O, M-Cl, M-Br, and M-F bond. The polarizability and the electronegativity, thereby the covalency of the bond are changed by the presence of other groups or atoms attached to the donor atom. The aforesaid statement is true only in those cases where the donor atoms are acting as ligands in the form of elementary ions. Generally the donor atoms (N and S) do not exist as elementary ions but in the combined state. This will make the electronegativity of the donor atoms different from that when they are present as elementary ions. Thus, inspite of decreased tendency of the electronegativity with the increasing atomic weight in a group, the covalent character of the bond may not increase with the atomic weight. In fact, no large variations are observed in the bonding

energy of the metal atoms with the heavier members of sulphur group and this effect is so prominent that for the heavy members of the nitrogen group the reverse sequence $P > As > Sb$ holds.²⁰ (Fajan²¹ argues that the relative polarity of the two adjacent bonded atoms depends not only on the polarization properties of the two bonded atoms, but also on the quantization. A different quantization of a particular atom can lead for the same two bonded atoms, two relative polarities A^+B^- as well as A^-B^+).

Another factor influencing the coordinating ability of the ligand is its total dipole moment ($\mu = P + \alpha E$, where P is permanent dipole moment; α , the polarizability and E , the field strength. Higher the dipole moment, higher is the coordinating ability). Thus, in spite of higher polarizability of sulphur in H_2S , compared to R_2S , the latter has a greater coordinating ability than H_2S due to the higher dipole moment of R_2S . Also the coordinating ability of H_2S is much lower than that of H_2O ($\mu_O \gg \alpha_S$)²² in spite of the higher polarizability of the sulphur compared to oxygen. Thus, H_2S will be bonded preferentially to cations having high field strength (high charge) while with low field strength, the reverse will hold.

Besides, the effect of polarizability on the type of bond formation between donor and acceptor^{and} influence of low lying d-orbitals capable of forming $d_{\pi} - d_{\pi}$ bonds on donors such as S, Se, Te, P, As, Sb etc. also deserve some discussion. If the metal ions have electrons in the d-orbitals, they may have a strong tendency to form

a bond of an order higher than one by back donation. However, this type of back donation is not possible with those metal ions having no or only a few electrons in the d-orbitals and also with O, N, F containing ligands (Ahrland¹³ has pointed out that the presence of filled or nearly filled d-orbitals is one of the conditions for effective back-donation). Such π -back bonding could easily explain the large difference between the affinities of the transition metal ions of the latter half of the periodic table, for the first donor atoms of each group (N, O, F) and for the second third etc., donor atoms of the same group (S, Se, Te, P, As etc.) having low lying vacant d-orbitals.^{13,23-25} This difference in the affinities is far greater than is expected from the increase of the polarizability alone. The presence of π -back bonding is still an unsettled problem.

The effects of the decrease in the polarizability and the number of lone pairs on the sulphur atoms in the order $S^- > RS^- > R_2S$ should also be taken into account on the bonding properties of the sulphur as donor.²⁶ Williams²⁷ considers that the principal difference between thiols and thioethers as ligands is that in the former sulphur is more polarizable but not as effective d_{π} -electron acceptor as the latter.

Taube²⁸ has shown that it is the back bonding between metal and ligand atoms which is responsible for the difference in the stability of complexes with ligands having F, O, N on the one hand and S, P, Se on the other.

From the above discussion it appears that in complexes formed by ligands containing N, O or F, the bonding should be mainly ionic in contrast to that in the complexes formed by coordinating with heavier donor atoms (S, Se, P etc).

RELATIVE AFFINITIES OF METAL IONS FOR SULPHUR

The effect of the metal ion on metal-sulphur σ -bond will depend on the ionization potential, electron affinity and the ionic (or covalent) radius of the metal ion. If the metal-sulphur bond is formed in solution by replacement of one ligand by another, the solvation energy also plays an important part in the formation of the compound due to different ΔG (free energy change) values in the gas and the solid phases. Besides, the strength of the metal-sulphur bond will also be affected by the presence of the non-bonding electrons in the low lying orbitals on the metal ions.

Earlier, Coats²⁹ and Williams,³⁰ Carleson and Irving³¹ tried to arrange the metal ions into groups according to the affinity for O, S...., and halides. It was first in 1958 when Ahrlund, Chatt and Davies¹³ divided the metal ions into two classes; (1) class 'a' metal ions which form the most stable complexes with the first atoms of each group (O, N, F), (2) class 'b' metal ions which form the most stable complexes with the second or subsequent atom, in aqueous solution.

For class 'a' metals the sequence in the stability of the complexes occurs as $O \gg S > Se > Te$. For class 'b' metals the sequence

$S \gg 0$ occurs, but any sequence can occur between S, Se and Te. In all the complexes the stability was measured by free energy change of a reaction, usually quoted just as an equilibrium constant, without any regard to solvent. It was stated that class 'b' cationic acceptors (in water) in their normal valence states form a more or less triangle with somewhat diffused border in the particular part of the periodic table. The base of the triangle stretches in the sixth period (from about tungsten to polonium) and it has its apex in the first period at copper as given in Fig. 1. Coordination of C_2H_4 , CO, CNR occurs only with metals of pronounced b-character. Ahrlund and coworkers¹³ proposed that this order of affinity of class 'b' metal ions depends on the availability of electrons in (n-1)d orbitals of the metal for π -bonding. The general idea that the π -bonding from metal ions to halides is important has been criticized by many workers.³²⁻³⁴ Various workers³²⁻³⁶ have given different explanations for 'a' and 'b' type of behaviour towards halides which could be extended to sulphur.

Pearson classified metal ions³⁷⁻³⁹ and ligands into hard and soft Lewis acids and bases. This classification of metal ions is similar to that, by Ahrlund, Chatt and Davies.¹³ The experimental observations suggest that hard acids combine preferentially with hard bases and vice-versa. The explanation^{24,38} for this observation, given by Pearson, includes: (a) various degree of ionic and covalent bonding, (b) π -bonding, (c) electron correlation phenomenon, (d) solvent effect, and (e) van der Waals forces.

Williams and Hale⁴⁰ deplored the quantitative notion of hard and soft acids and bases. They believe that the a/b classification is little more than a reflection of σ -bonding and the gross controlling factor of the classification is clearly the relative importance of ionic and covalent bonding which has been measured by the value of $1/(I.P. \times r_e)$, where I.P. is the ionization potential of the acceptor and r_e the metal ligand bond distance. The higher the value of this function, the higher is the ionic character of the bond. The percentage ionic character, when an acceptor of one type goes over to an acceptor of the other depends upon the charge, the type of the reactants and the solvent (ligand) bound to them. They further believed that London energies and classical polarization are also important to some degree, but as with π -bonding no quantitative demonstration of these effects has been done.

Jørgensen⁴¹ classified the class 'b' metal ions into three types: (i) metals with unusually low oxidation numbers, (ii) metals with certain high oxidation numbers, (iii) s^2 family e.g. Sn(II), Sb(III), Tl(I), Pb(II), and Bi(III). There are some metal ions which show 'b' character in high and low oxidation states and 'a' character in intermediate oxidation state, e.g., Mn.

In general, there seems to be an increase in class 'b' character for ions of A-groups in the periodic table ($IA < IIA < IIIA$) and this is also true in the B-groups ($Ag^+ < Cd^{+2} < In^{+3}$). However, for any one element, the series is quite unpredictable e.g.,

$\text{Cu(I)} < \text{Cu(II)}$, $\text{Tl(I)} > \text{Tl(III)}$, $\text{Sn(II)} < \text{Sn(IV)}$, $\text{Pt(II)} > \text{Pt(IV)}$ in class 'a' character. The class 'a' or 'b' character seems to depend upon the relative magnitudes of electron affinities of the cations, exposure of the relevant orbitals (overlap), interatomic distance, charge, and cation polarizability.

In order to explain class 'a' and 'b' character, Jørgensen⁴¹ pointed out that the electric dipole polarizability is connected partly with a few of the continuum orbitals and partly with valence orbitals. If the simultaneous formation of σ -bonds in the direction from X(=S) to M and the back bonding in the opposite direction is connected, not with definite, discrete, empty orbitals of X, but with the continuum, it is reasonable to think of M being polarized by X. The population of X(=S) is expected to be more pronounced, the lower the ionization energy of X. The reason why the chemical softness of H(-1) , R_3P , R_2S and I(-1) might have something to do with empty orbital not present to the same degree in H_2O or F(-1) , is not a question of π -back bonding to 3d orbitals of R_3P , R_2S and I(-1) , but a question of continuum starting at lower energy in these ligands compared to analogous R_3N , R_2O and F(-1) . Recently G. Klopman⁴² elaborated his theory for heteronuclear molecules⁴³ to a second order perturbation formula reproducing, with exception of H^+ , the Ahrland, Chatt and Pearson's series of hard and soft central atoms. $\text{Al(III)} > \text{La(III)} > \text{Be(II)} > \text{Mg(II)} > \text{Ca(II)} > \text{Fe(III)} > \text{Sr(II)} > \text{Cr(III)} > \text{Ba(II)} > \text{Ga(III)} > \text{Cr(II)} > \text{Fe(II)} > \text{Li(I)} > \text{Ni(II)} > \text{Na(I)} > \text{Cu(II)} > \text{H}^+ > \text{Tl(I)} > \text{Cd(II)} > \text{Ag(I)} > \text{Tl(III)} > \text{Au(I)} > \text{Hg(II)}$.

From his calculations he concluded that soft-soft interaction results essentially in covalent bonding between an empty and filled orbital of comparable energy whereas hard-hard interactions are charge controlled and determined by Medalung potential. In this treatment he has taken into account the solvation energy which modifies very strongly the order of softness and it is quite conceivable that it will be highly solvent dependent (acids with high oxidation numbers thus become relatively softer in non-polar solvents e.g., Te(IV) coordinates diarsine (soft-base) in dioxane more strongly than Fe(III) and Cr(III)).⁴⁴

Drago and Weyland⁴⁵ suggested an empirical equation to correlate the heat of formation of acid-base complexes such as:

$$-\Delta H = E_A E_B + C_A C_B$$

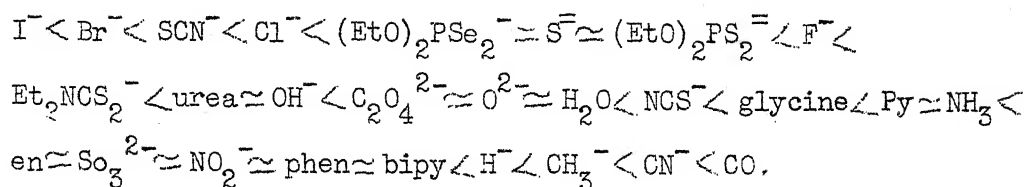
where E terms represent the susceptibility of the acid or the base to undergo electrostatic interaction and C terms represent their ability to participate in covalent bonding.

Ahrland⁴⁶ has pointed out that the hard-hard interactions are generally endothermic while in the soft-soft interaction heat is evolved, which corresponds to the actual covalent bond energy with a much smaller entropy change.

Thus, from the above discussion it appears that most probably the hard-hard interaction is mostly ionic, while the soft-soft one is of covalent type which is variable from one case to another. Further,

the role of π -back bonding in the soft-soft interaction is still undecided.

In the spectrochemical series given below the position of sulphur varies with the ligand:

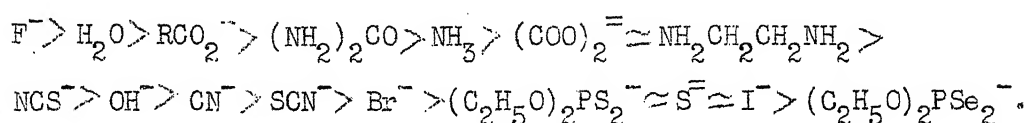


(where Py = pyridine; en = ethylenediamine; bipy = 2,2'-bipyridyl; phen = 1,10-phenanthroline).

As $\Delta/\Delta_0 = f(\text{ligand}) \times g(\text{metal ion})^{47}$ is the difference between the σ -antibonding effect on the higher sub-shell (e.g. in octahedral chromophore, MX_6 , t_{2g} in tetrahedral chromophore, MX_4) and the π -antibonding effects on the lower sub-shell (t_{2g} or e_g respectively), one can rationalize that the ligands containing one lone pair, such as H^- , NH_3 , SO_3^{2-} form only σ -bonds and have large values of Δ . On the other hand, ligands with several lone pairs have also π -bonding effects on the partially filled shell of the metal ion and thus decrease Δ ; $(\text{C}_2\text{H}_5)_2\text{PS}_2^- < (\text{C}_2\text{H}_5)_2\text{NCS}_2^- < (\text{C}_2\text{H}_5)\text{OCS}_2^-$. This effect has also been observed in sulphur containing ligands by Jørgensen;²⁶ $\text{dtp}^- < \text{exen} < \text{dte}^- < \text{dmp} < \text{thioglycollate} < \text{dithiomalate} < \text{amines}$.

As discussed above, one should expect that metal-sulphur bond should have a high percentage of covalency and this is even more pronounced if the sulphur is attached to a 'b' type of metal ion.

The nephelauxetic series⁴⁸⁻⁵⁰ is a measure of covalent tendency in a particular bond formed between the ligands and metals. Thus, the sulphur ligand should have high nephelauxetic effect. However, the data are not sufficient to ascertain this. The positions of some of the sulphur ligands in the above series (in which the ligand are arranged in the decreasing order of β) are shown below:



It will be interesting to note that this series follows roughly the order of decreasing electronegativity: $F > O > N > Cl > Br > S \approx I > Se$.

The trans effect depends upon the permanent dipole moment, the induced dipole moment, the polarizability, the charge, the size of the ligand and the degree of π -bonding in a particular bond. The dependence of trans effect on the degree of π -bonding has been criticized by William^{30,32} and Venanzi¹⁷ (non π -bonding ligands activate the trans position by polarization and σ -covalent bonding). This effect should be very strong in sulphur ligands^{23,51,52} due to large polarizability of sulphur. Although Chatt, et al.,^{53,54} have suggested a relative order of the strengths of trans effect among a number of various ligands, many of the data are based on the relative yields obtained under different sets of conditions. But in a complex the presence of a strong trans-directing ligand may influence the trans directive nature of the other ligands and so the

position of sulphur ligands compared with other ligands having a strong trans-directing influence may vary considerably according to the particular system being studied. This makes the situation complex and necessitates further study before drawing some conclusions.

As the present thesis describes the complexing behaviour of ligands containing the $\text{>N}-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}=\text{S}$ and $\text{S}^--\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}=\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\text{S}^-$ groups, a brief review of the earlier work⁵⁵⁻⁵⁷ with ligand containing the same groups will not be out of place here. Thus, after general considerations of the nature of M-S bond described in the preceding paragraphs, a review of the available literature on complexing behaviour of ligands containing the $\text{>N}-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}=\text{S}$ and $\text{S}^--\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}=\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\text{S}^-$ groups is presented here.

THIOUREA AND ITS DERIVATIVES

The donor site in thiourea and its derivatives can either be sulphur or nitrogen or both depending on whether it acts as monodentate or bidentate. In general, it acts as monodentate ligand and bonding in complexes⁵⁸⁻⁶⁸ takes place through sulphur atom, not only with class 'b' metal, but class 'a' metal ions as well. However, the infrared spectral measurements indicate that the ligand is coordinated through nitrogen in $\text{Ti}(\text{tu})_2\text{Cl}_4$.⁶⁹ The nature of bonding in thiourea complexes can either be ionic or covalent⁷⁰⁻⁷² depending on the metal ions forming the complexes. The ionic complexes can either be 1:4 or 1:6 types. In these ionic complexes the polarizable thiourea molecules act as bridges between separated cations and anions.

The main cohesive forces are due to ion dipole interactions. Although cations and anions are contained in channels of thiourea molecules, these thiourea molecules are not bound to one another as they are in the thiourea hydrocarbon channel inclusion complexes.⁷³ The structures of these complexes have been determined.⁷²⁻⁷⁴

The stereochemistry of the complexes as determined by the structure of a number of covalent bonded thiourea complexes⁷³⁻⁸⁴ is either square-planar or octahedral. Lopez-Castro and Truter⁷⁴ examined the crystal structures of both high and low-spin Ni(II) complexes, and found that in diamagnetic complexes Ni-S bond distance is 2.1 - 2.3 Å, whereas in the six coordinated complexes it is 2.4 - 2.6 Å. This has also been found in octahedral $[\text{Ni}(\text{tu})_2(\text{NCS})_2]$ ⁸⁴ complexes. The compounds $\text{M}(\text{tu})_2(\text{NCS})_2$, where M = Mn, Co, or Cd, are isostructural with $\text{Ni}(\text{tu})_2(\text{NCS})_2$, but the zinc complex $\text{Zn}(\text{tu})_2(\text{NCS})_2$ ⁸⁵ is not. In the $[\text{Ni}(\text{Py})_2(\text{tu})_2\text{ClO}_4]$, the sulphur atoms of the two thiourea molecules probably act as bridges.⁸⁶ The structures of monothiourea cadmium sulphate dihydrate⁸⁷ and bis-thiourea cadmium-nitrate⁸⁸ complexes have also been determined. The complex $\text{Cd}(\text{tu})_2\text{Cl}_2$ is tetrahedral, but $\text{Pb}(\text{tu})_2\text{Cl}_2$ has a polymeric structure in which the lead atom is seven coordinated, surrounded by four bridging sulphur atoms at distance 2.9 - 3.1 Å and two chlorine atoms at 3.2 Å while the non-bridging chlorine is at a distance of 2.75 Å from the central metal ion.⁷⁰ The complex $[\text{Pb}(\text{tu})_6](\text{ClO}_4)_2$ ⁸⁹ is a distorted octahedral, whereas $[\text{Pb}(\text{tu})_4](\text{Picrate})_2$ ⁹⁰ has a polymeric structure in which the lead atom

is hexa coordinated. The distance from lead to sulphur is in the same range as in $\text{Pb}(\text{tu})_2\text{Cl}_2$ complex. In $[\text{Te}(\text{tu})_4]\text{Cl}_2$ ⁹¹ tellurium has square planar arrangement. Magnetic, spectrophotometric and infrared studies⁹² on thiourea complexes of some salt of Co^{+2} , Zn^{+2} and Cd^{+2} with oxyanions, having general formula $[\text{M}(\text{tu})_m\text{X}_n]$, have been investigated. On the basis of i.r. studies ($150\text{ cm}^{-1} - 400\text{ cm}^{-1}$) it has been possible to distinguish between tetrahedral, square planar and octahedral coordinations around the metal ion. The preparation and structural studies of cobalt(II) salt-thiourea complexes have been reported by Carfagno.⁹³

Thiourea forms complexes of the type^{94,95} $\text{Rb}(\text{tu})_4\text{I}$, $\text{Au}(\text{tu})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4, \text{BF}_4$ and CF_3COO) with rubidium(I) and gold(I) respectively whereas ethylene thiourea⁹⁶ with tin(IV) and titanium(IV) forms complexes of the type $\text{M}(\text{etu})_2\text{X}_4$ ($\text{X} = \text{Cl}, \text{Br}$ or I). In the complex⁹⁴ $\text{Rb}(\text{tu})_4\text{I}$, the average Rb-S separation is 3.53\AA and S-S separation is 4.15\AA . Comparison of the Rb-S and S-S separation for $\text{Rb}(\text{tu})_4\text{I}$ with those of the respective Tl and Cs complexes indicate that the cohesive forces in these complexes are mainly electrostatic. Infrared studies^{95,96} on gold(I), titanium(IV) and tin(IV) complexes indicate that the bonding in Au(I) complexes, is through sulphur while in tin(IV) and titanium(IV) complexes, through nitrogen atoms. Molecular weight and conductivity studies⁹⁶ on nitrogen bonded complexes indicate them to be monomeric molecular addition type. The thiourea complexes of rhenium and technetium (in solution) have

been described by various workers⁹⁷⁻¹⁰¹ in three and five oxidation states. The infrared spectrum of $[\text{Re}(\text{OH})_2(\text{tu})_4\text{Cl}_3]$ has also been studied.¹⁰⁰ Formation of its complexes with rhenium(IV) and ruthenium(III) in hydrochloric acid have also been observed^{102,103} and stoichiometries of Ru(III) complexes as $[\text{Ru}(\text{H}_2\text{O})\text{tuCl}_4]^-$, $[\text{Ru}(\text{H}_2\text{O})(\text{tu})_2\text{Cl}_3]$ and $[\text{Ru}(\text{H}_2\text{O})(\text{tu})_3\text{Cl}_2]$ have been confirmed by their absorption spectra and optical density measurements. The equilibrium constants for the formation of chloro(thiourea)rhenium(IV) complex have been calculated by ion exchange method.¹⁰³

In $\text{Mo}_2(\text{tu})_3\text{Cl}_6$, octahedral coordination with a metal-metal interaction^{104,105} is proposed on the basis of magnetic moment data. The thiourea-lanthanide acetate complexes have also been studied.¹⁰⁶ A recent thermodynamic study¹⁰⁷ shows the formation of four successive complexes with Ag^{+1} ion. It has also been found that complexes of the type $\text{M}(\text{tu})^{+2}$, $[\text{M}(\text{tu})_2]^{+2}$, $[\text{M}(\text{tu})_3]^{+2}$, $[\text{M}(\text{tu})_4]^{+2}$ and $[\text{M}(\text{tu})_6]^{+2}$ where $\text{M} = \text{Pb}$ or Cd are formed in aqueous dioxane and were studied by polarographic method.¹⁰⁸ The substitution reactions of thiourea complexes, $\text{Zn}(\text{tu})_2\text{Cl}_2$, $\text{Ni}(\text{tu})_4\text{Cl}_2$, $\text{Cu}(\text{tu})\text{Cl}$, $\text{Cu}(\text{tu})_3\text{Cl}$, $\text{Ag}(\text{tu})_3\text{NO}_3$ and $\text{Pd}(\text{tu})_4\text{Cl}_2$ with anhydrous ammonia give rise to corresponding amines.¹⁰⁹ Recently¹¹⁰ the studies on trans-dioximato complexes of Co(III) of the type $[\text{Co}(\text{DH})_2(\text{seu})(\text{thio})]\text{Cl} \cdot \text{H}_2\text{O}$; $[\text{Co}(\text{DH})_2(\text{seu})(\text{thio})]$ $[\text{Co}(\text{DH})_2(\text{seu})(\text{thio})]\text{I}$ and $[\text{Co}(\text{DH})_2(\text{seu})(\text{thio})]\text{NO}_3 \cdot \text{H}_2\text{O}$ having thio-Co-seu bond indicate that in the dioximato complexes of cobalt(III), the trans influence of selenourea (seu) is much greater than that of the thiourea

Raman and i.r. spectra, magnetic anisotropies and powder susceptibilities of $\text{Ni}(\text{tu})_4\text{Cl}_2$ have been studied.^{111,112}

N,N'-DISUBSTITUTED THIOUREA

Extensive studies¹¹³⁻¹²⁹ have been done on the behaviour of N,N'-disubstituted thioureas. Cu^{+1} and Ag^{+1} give complexes with 1,2,3 and 4 molecules of ethylene thiourea. The complexes of Ni(II) occur with tetrahedral, octahedral and tetragonal coordination.^{113,119-123} It appears that the anion plays a prominent role in determining the stereochemistry of Ni(II) in substituted thiourea complexes. Thus, $\text{Ni}(\text{etu})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) are octahedral and have been isolated in cis and trans forms, but $\text{Ni}(\text{etu})_4\text{I}_2$ is six coordinated and also diamagnetic while $[\text{Ni}(\text{etu})_4](\text{ClO}_4)_2$ is diamagnetic and square planar.^{120,121} It is possible that Ni(II) may attain a variety of stereochemical environments with the same donor atom but such complexes are rare. With 1-(1-naphtyl)-2-thiourea, Ni(II) gives tetrahedral and with ethylene thiourea it gives octahedral, diamagnetic planar and diamagnetic tetragonal complexes. In acetone solution dissociation of octahedral $(\text{NiL}_6)^{+2}$ to tetrahedral $(\text{NiL}_4)^{+2}$ where L = ethylene thiourea, N,N'-diethylthiourea, N,N'-di-n-butylthiourea, N,N'-diallylthiourea, N-phenylthiourea and N,N'-diphenylthiourea occurs and it was shown that this type of dissociation is favoured at low temperature.¹³⁰ Co(II) is reported to exhibit generally tetrahedral coordination¹²⁹ but has a strong tendency to form penta coordinated adduct.^{124,125,127}

N,N'-dicyclohexyl thiourea and N,N'-diphenyl thiourea form tetrahedral complexes with Co^{+2} in organic solvents,^{115,118,119} but ligands undergo structural changes in solution affecting coordinating tendencies.

In solid state, N,N'-dicyclohexyl thiourea forms the octahedrally coordinated complexes CoL_6X_2 , (where $\text{X} = \text{NO}_3, \text{ClO}_4$). There are rare complexes of octahedrally coordinated Co^{+2} containing all unidentate sulphur ligands. Spectrochemical investigations on tetrahedral complexes¹³¹ CoL_2X_2 and ZnL_2X_2 where L = substituted thiourea and X is halogen have shown the presence of intramolecular hydrogen bonding interaction between NH groups and the halogen. Presence of such hydrogen bonding in dichloro bis(diethylthiourea)Zn(II) has been shown by X-ray analysis of the crystal.¹³²

Studies of the Co(II) and Ni(II) complexes of N-amidine-S-ethyl-thiourea indicate that these are square planar and isostructural.¹³³ Bis-chelated complexes of Co(II), Ni(II), Cu(I), Zn(II), Cd(II), Hg(II) and Bi(III) with 1-allyl-3-(2-pyridyl-1)-2-thiourea¹³⁴ and the complexes of Cu(I), Hg(II), Pd(II), Pt(II) and Rh(III) with N,N'-bis(2-pyridyl)thiourea¹³⁵ have been studied. Similar studies¹³⁶ on Co(II), Ni(II), Pd(II), Cd(II), Hg(II), Cu(I), and Bi(III) complexes of 1-phenyl-3-(2-pyridyl)-2-thiourea show that both pyridyl nitrogen, and sulphur in the ligand act as coordination sites in the complex formation. Similarly 1-(2-pyridyl)-2-thiourea has also been used as a polydentate ligand in the preparation of several metal complexes.¹³⁷ Crystal structure¹³⁸ of $\text{Ni}(\text{NCS})_2[\text{S}=\text{C}(\text{NHEt})_2]_4$ has been determined in which the ligands are octahedrally arranged. NCS ion is bonded to

metal through nitrogen ($\text{Ni-N}=1.993\text{\AA}$). Thiourea unit is bonded through sulphur ($\text{Ni-S}=2.493\text{\AA}$). There are evidence of the presence of (a net work) inter- and intramolecular $\text{N-H}\cdots\text{S}$ hydrogen bonds. Crystal structure¹³⁹ of chloro-tris(N,N -dimethyl thiourea)copper(I) shows its tetrahedral structure. X-ray structural studies on dichloro-bis(diethyl-thiourea)-zinc(II) has also been done.¹³²

Carlin and Holt,¹⁴⁰ by their studies on ethylene thiourea and N,N' -disubstituted thiourea complexes of Co(II) indicated a higher position of ethylene thiourea, in spectrochemical series than R_2S . The value of B is found to be 66% of the free ion value. In nephelauxetic series, the position of thiourea is approximately equal to that of iodide ion.¹¹⁸

Trimethylene thiourea has been studied by various workers^{74,117} and the crystal structure of Ni(II) complex has been investigated by Luth and Truter.¹⁴¹

Recently new thiourea derivatives¹⁴² 3-diphenylphosphinothioyl-1-phenylthiourea, 3-diphenylphosphinothioyl-1,1-diethylthiourea and 3-diphenylphosphinothioyl-1,1-dimethylthiourea were found to behave as bidentate ligands with Ni(II) , Pd(II) , Co(II) and Cu(II) . These ligands are found to be sulphur donor.

1-(2-pyridyl)-2-thiourea¹⁴³ is a bidentate ligand. The Ni(II) , Co(II) , chloride, bromide, and perchlorate complexes of this are reported. The infrared, the visible, (solid and solution) and the

u.v. spectral, the magnetic and conductance data indicate the nickel complexes in three configurations, tetrahedral, planar and octahedral. Equilibria $\text{NiL}_3^{+2} \rightleftharpoons \text{NiL}_2^{+2} + \text{L}$ and $3\text{NiL}_2^{+2} \rightleftharpoons 2\text{NiL}_3^{+2} + \text{Ni}^{+2}$ are found in solutions. The position of the ligand in the spectrochemical and nephelauxetic series is confused one.

Infrared and electronic spectral studies¹⁴⁴ on the complexes of the type $\text{MX}_4 \cdot 2\text{L}$ ($\text{M} = \text{Sn(IV)}$ and Ti(IV) , $\text{X} = \text{Cl, Br, I}$ and $\text{L} = \text{N-allyl-thiourea}$) indicate that the coordination takes place through nitrogen. This type of coordination were also found in ethylene thiourea Ti(IV) and Sn(IV) halide complexes.⁹⁶ Polarographic studies¹⁴⁵ on the complex formation by cadmium ion with allylthiourea in aqueous and water-ethanol medium indicate the ease of formation by increase of concentration of non-aqueous solvent in the solution.

The formation of ruthenium(III) complexes¹⁰² with phenylthiourea, diphenylthiourea, di(o-tolyl)thiourea, and di-(p-tolyl)-thiourea (blue complexes) and hydroxymethylthiourea (blue-violet) have been investigated by absorption spectra and optical density measurements in aqueous alcoholic medium (40 vol.%).

Recently¹⁴⁶ nuclear magnetic resonance studies on tetrahedral Co(II) complexes have been done. The origin of the large isotropic shifts have been discussed in detail.

THIOSEMICARBAZIDE

Thiosemicarbazide can act as a neutral or a charged species. The inner complexes of Ni(II) , Pd(II) and Pt(II) were prepared and

isolated in the cis and trans forms.^{147,148} In the trans square-planar complex, $\text{Ni}(\text{CH}_4\text{N}_3\text{S})_2$, there is a complete localization of the double bond between carbon and nitrogen, indicating predominance of the thiol form. The other isomer is diamagnetic but the structure determination is not possible.^{150,151} While the green compound $\text{Ni}(\text{HTSC})_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ is found to have square planar trans-configuration with coordination occurring through S-atom and terminal nitrogen.¹⁴⁹ Similarly, the cis and the trans forms of Co(III) complexes¹⁵² have been isolated. Cobalt(III) complexes of thiosemicarbazide derivatives (R thiosh)¹⁵³, where $\text{R} = \text{C}_6\text{H}_5$ or $\text{CH}_3\text{C}_6\text{H}_4$ with the composition $[\text{Co}(\text{DH})(\text{R thiosh})_2]\text{Cl}_2$, $[\text{CoCl}_2(\text{DH})(\text{R thiosh})]$ and $[\text{Co}(\text{R thiosh})_3]\text{Cl}_3$ have been studied. Potentiometric titration indicates that complex $[\text{Co}(\text{DH})(\text{R thiosh})_2]\text{Cl}_2$ is a diacid whereas $[\text{Co}(\text{R thiosh})_3]\text{Cl}_3$ is a tribasic acid (DH = dimethylglyoxime). The series of copper complexes, $\text{Cu}(\text{thioisosemicarbazide})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \frac{1}{2}\text{SO}_4$) and $\text{Cu}(\text{thiosemicarbazide})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{ClO}_4, \frac{1}{2}\text{SO}_4$) have been prepared.^{152,154} The former series has been shown to have polymeric square-planar structure while the latter series has distorted octahedral structure. Nickel forms square-planar complexes¹⁵⁵ of the type $\text{Ni}(\text{CN})_2(\text{thiosemicarbazide})_2 \cdot \text{H}_2\text{O}$. Pt(II), Pd(II) and Ni(II) form square planar complexes.¹⁵⁶ Both cis and trans geometric isomers have been obtained with the general formula, $[\text{M}(\text{HTSC})_2]^{+2}$ ¹⁵⁷ while only trans form was obtained for the neutral species $[\text{M}(\text{TSC})_2]$.¹⁵⁸ Infrared and the reflectance spectral studies were made, but X-ray structure determinations have been carried

out on Ni(dithiosemicarbazide-sulphate) trihydrate, β -nickel-dithiosemicarbazide-sulphate and tris-thiosemicarbazide-nickel dinitrated only.¹⁵⁹⁻¹⁶²

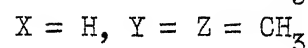
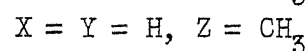
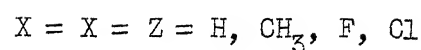
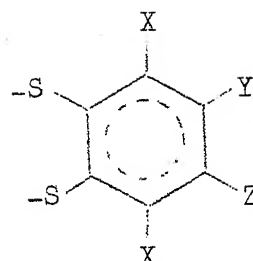
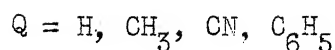
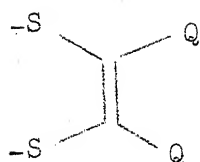
Tetrahedral complexes of Pt(IV) with 1-phenylthiosemicarbazide have also been prepared.¹⁶³ The complexes of most of the class 'b' ions with a few derivatives of semicarbazide (derivatives with Schiff's bases),^{164,165} and salicylaldehyde thiosemicarbazide (octahedral) derivatives¹⁶⁶ have been prepared.

Recently¹⁶⁶ a series of new ligands have been prepared by reacting aliphatic and aromatic aldehydes with ethylene thiosemicarbazide. These compounds form 1:1 complexes with Cu(II). These are paramagnetic and a structure has been proposed involving bonding between two thiocarbonyl sulphurs of the ligands.

The stability constants and the heats of formation¹⁶⁷ of complexes with divalent alkaline earths, Zn(II), Co(II), and Mn(II) have been determined. Nuclear γ -resonance studies¹⁶⁸ on the high spin iron(II) complexes of thiosemicarbazide (HthSC) of the type $\text{FeX}_2(\text{HthSC})_2 \cdot n\text{H}_2\text{O}$ indicate these complexes are octahedral and commented that among all the iron compounds known at present, the complex $\text{FeSO}_4(\text{HthSC})_2 \cdot 1/2\text{H}_2\text{O}$ has the greatest quadrupole splitting.

1,2-DITHIOLENE COMPLEXES

Complexes of the 1,2-dithiolene ligand systems, which are illustrated as below, have been studied extensively in the last

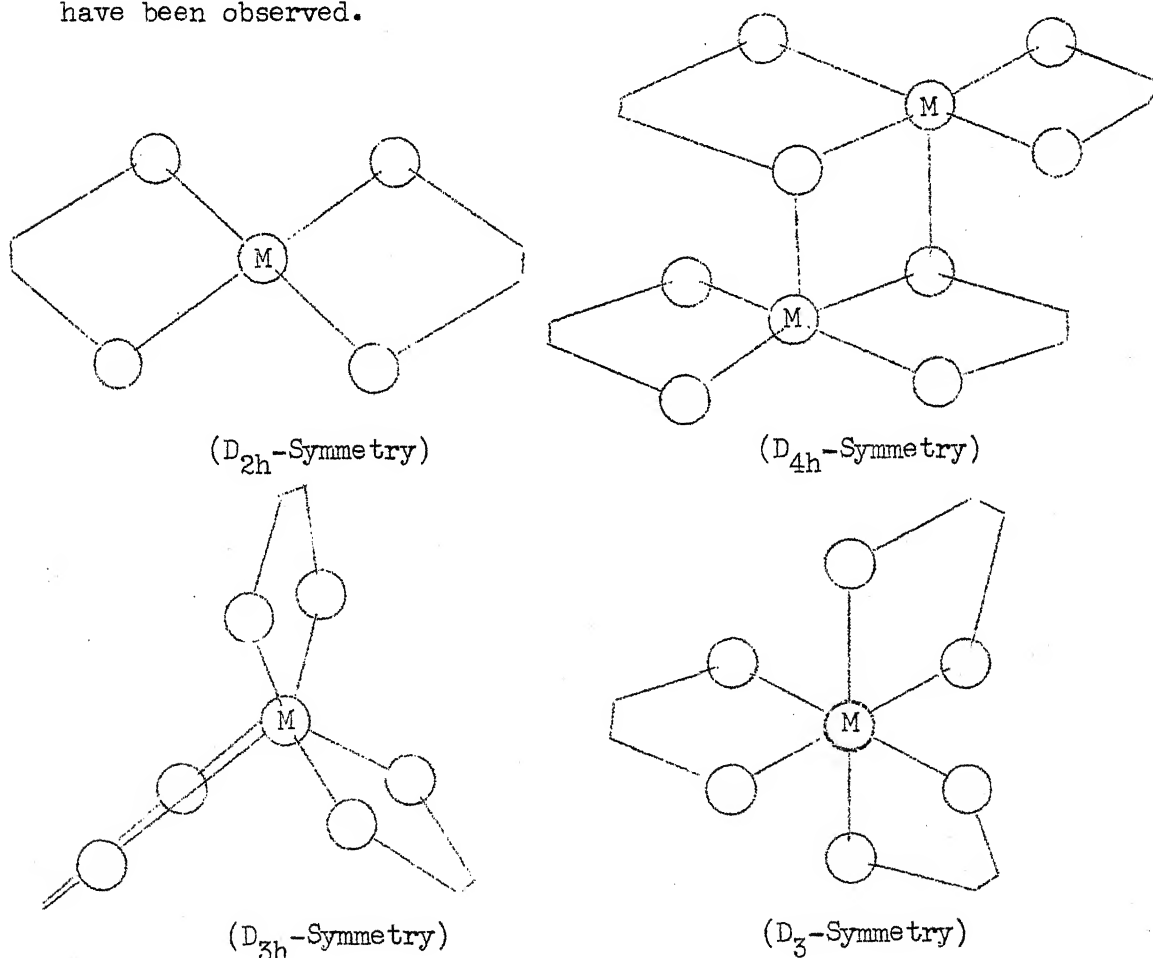


decade.^{55-57,169-174} The comprehensive studies of the bis-complexes are described in a number of recent reviews and references therein.¹⁷⁵⁻¹⁸² The first report of a six-coordinate tris complex containing the 1,2-dithiolene ligand systems was made by King,¹⁸³ who obtained $Mo(S_2C_2(CF_3)_2)_3$ and its W analog from the reaction of the corresponding hexacarbonyl with the heterocyclic compound bis(trifluoromethyl)dithietene. Subsequent studies of the tris complexes¹⁸⁴⁻¹⁸⁶ were considerably influenced by structural work which disclosed a number of the tris complexes to possess the unexpected and the highly unusual trigonal prismatic coordination.¹⁸⁷⁻¹⁸⁹

The avid interest in the 1,2-dithiolene complexes probably stems from the following factors. (a) Both the bis and the tris-complexes undergo easily reversible oxidation-reduction reactions. (b) The 1,2-dithiolene ligand systems appear to stabilize the square-

planar geometry for a wide variety of metal ions. (c) Many of the six-coordinate tris-complexes possess the highly unusual ^{trigonal}/prismatic coordination. (d) The electron-withdrawing nature or π -acidity of the ligands in the bis and tris complexes can be varied by employing ligands with different substituent groups.

With "pure" dithiolene complexes in which no other coordinating ligands are present, the following four definite structure types have been observed.



The bonding in these compounds can be explained within the concepts of the simple M.O. and valence-bond theories, provided that

the π -delocalized nature of the ligands and the high covalency of the complexes are adequately taken into account.¹⁷⁰

There have been over twenty complete structure^{187-189,190-211} determinations on complexes containing 1,2-dithiolene ligands, including a large number in which the metal is coordinated solely by the dithiolene ligand systems.

The following paragraphs presents a brief review of the complexing behaviour of these ligands in the last two years (1970-72), since before this period, excellent reviews have appeared in various books.^{169,170,212,213}

The complexes of indium(III) with toluene-3,4-dithiolate(A) and 1,2-dicyanoethylene-1,2-dithiolate(A) (InA_2)⁻, (InA_3)⁻³ have been described.²¹⁴ X-ray structural investigation^{215,216} showed that the anion with A = 1,2-dicyanoethylene-1,2-dithiolate, involves six-coordinated indium. These compounds form an interesting groups of four-five and six-coordinate indium complexes, which undergo polarographic reduction in non-aqueous solution corresponding formally to the one-electron reduction step $\text{In}^{\text{III}} \rightarrow \text{In}^{\text{II}} \rightarrow \text{In}^{\text{I}} \rightarrow \text{In}^0$. Further studies on indium complexes by D.G. Tuck et al.,²¹⁷ revealed that indium(I) halides react with 1,2-bis(trifluoromethyl)dithitene(L) to yield the complexes InLX (X = Cl, Br or I) which they believed to be polymeric indium(III) dithiolato complexes. Reaction of these complexes with dimethyl sulphoxide (dmsO) gave $[\text{InL(dmsO)}_4]\text{X}$. With 2,2-bipyridyl (= bipy) or 1,10-phenanthroline, the product was an ionic

dimer of the type $[\text{InL}(\text{bipy})_2][\text{InL}_2(\text{bipy})]$. Spectroscopic and polarographic evidences were presented to support the formulation of all these complexes. Toluene-3,4-dithiol(A) also forms complexes²¹⁸ with tin, arsenic, antimony and bismuth of the types $(\text{MA}_2)^-$ ($\text{M} = \text{As}, \text{Sb}$ or Bi) and $(\text{MA}_3)^{-2}$ ($\text{M} = \text{Sb}$ or Sn). Molar conductance studies showed their electrolytic behaviour to be either 1:1 or 2:1 type. Magnetic susceptibility measurement²¹⁹ at higher temperature in solid and solution (3.14 B.M.) indicate that tetrabutylammonium bis(toluene-3,4-dithiolato)cobalt exhibit a triplet ground state, but behaviour of magnetic susceptibility²²⁰ at lower temperature (8°K) indicate the singlet ground state.

Disodium dicyanoethylene-1,2-dithiolate (Na_2mnt) forms complexes²²¹ with group IVB halides and acetates having stoichiometries $\text{M}(\text{mnt})_3^{-2}$ ($\text{M} = \text{Sn}(\text{IV})$ or $\text{Ge}(\text{IV})$), $(\text{Sn}(\text{mnt})_2\text{X}_2)^{-2}$ ($\text{X} = \text{Cl}, \text{Br}$ or I), $(\text{Pb}(\text{mnt})_2)^{-2}$ and $(\text{Pb}(\text{mnt})\text{Br})^-$. X-ray powder pattern indicate that $[(\text{Ph}_4\text{As})_2\text{Ge}(\text{mnt})_3]$ and $[(\text{Ph}_4\text{As})_2\text{Sn}(\text{mnt})_3]$ are isomorphous, and have octahedral configuration, lead(II) complex $[(\text{Bu}_4^{\text{n}}\text{N})_2\text{Pb}(\text{mnt})_2]$, is square-pyramidal and three coordinated lead(II) complexes e.g., $[(\text{Bu}_4^{\text{n}}\text{N})\text{Pb}(\text{mnt})\text{Br}]$ is tetrahedral. Spectral studies reveals that the π -donor ability of sulphur atoms is greater in the tris(mnt)-germanium than in tris(mnt)tin complexes.

Dimercaptomaleonitrile dianion(mnt) with unipositive cations Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ forms the complexes of the types $\text{Na}_2(\text{mnt}) \cdot 2\text{H}_2\text{O}$, $\text{Na}_2(\text{mnt}) \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Na}_2(\text{mnt})$, $\text{K}_2(\text{mnt}) \cdot \text{H}_2\text{O}$, $\text{K}_2(\text{mnt}) \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{K}_2(\text{mnt})$, $\text{Rb}_2(\text{mnt})\text{H}_2\text{O}$,

$\text{Rb}_2(\text{mnt})$, $\text{Cs}_2(\text{mnt})$, $\text{Cs}_2(\text{mnt}) \cdot \text{H}_2\text{O}$, $\text{Na}_4\text{Ti}_2(\text{mnt})_3 \cdot \frac{3}{2}\text{H}_2\text{O}$, $\text{Na}_4\text{Ti}_2(\text{mnt})_3$, $\text{Ti}_2(\text{mnt})$. These complexes have been investigated^{222,223} using thermooptic, T.G., D.T.A., i.r. and single crystal X-ray and powder diffraction techniques. A tentative assignments of the normal vibration of the dimercaptomaleonitrile and cyanodithioformate systems are given.²²³ X-ray studies indicate²²² that $\text{Na}_2(\text{mnt}) \cdot 2\text{H}_2\text{O}$, $\text{Na}_2(\text{mnt})\text{H}_2\text{O}$, $\text{Na}_2(\text{mnt})$, $\text{K}_2(\text{mnt})$, $\text{Rb}_2(\text{mnt})\text{H}_2\text{O}$ and $\text{Cs}_2(\text{mnt})\text{H}_2\text{O}$, are rhombic, $\text{Rb}_2(\text{mnt})$, $\text{Cs}_2(\text{mnt})$, monoclinic whereas $\text{Ti}_2(\text{mnt})$, hexagonal. Uranyl chelates of the ligand (mnt) having the stoichiometries^{224,225} $\text{A}_2[\text{UO}_2(\text{mnt})_2]$, where $\text{A} = \text{N}(\text{C}_2\text{H}_5)_4$ or $\text{N}(\text{n-C}_3\text{H}_7)_4$, $(\text{NEt}_4)_2[\text{UO}_2(\text{mnt})_2\text{OPy}]$, $(\text{NPr}_4)_2[\text{UO}_2(\text{mnt})_2\text{OPy}]$, $(\text{NEt}_4)_2[\text{UO}_2(\text{mnt})_2\text{OP}(\text{C}_6\text{H}_5)_3]$, $(\text{nPr}_4)_2[\text{UO}_2(\text{mnt})_2\text{OP}(\text{C}_6\text{H}_5)_3]$, $(\text{NEt}_4)_4[\text{UO}_2(\text{mnt})_2\text{OAs}(\text{C}_6\text{H}_5)_3]$ and $(\text{NPr}_4)_2[\text{UO}_2(\text{mnt})_2\text{OAs}(\text{C}_6\text{H}_5)_3]$ have been prepared and studied by usual techniques.

Transition metal dithiolene complexes of the type²²⁶
 $[\text{M}(\text{L})(\text{S-S})_2]^-$ ($\text{M} = \text{Fe}$ or Co ; $(\text{S-S}) = \text{S}_2\text{C}_2(\text{CN})_2$, $\text{S}_2\text{C}_2(\text{CF}_3)_2$ or $\text{S}_2\text{C}_6\text{Cl}_4$;
 $\text{L} = \text{o-C}_6\text{H}_4(\text{AsMe}_2)_2$, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{-AsMe}_2$, cis- $\text{Ph}_2\text{PCH:CHPPh}_2$, Me_2PhP , or Me_2PhAs), $[\text{M}(\text{L})(\text{S-S})_2]^0$ ($\text{M} = \text{Fe}$, or Co ; $(\text{S-S}) = \text{S}_2\text{C}_2\text{Ph}_2$; $\text{L} =$
 $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ or Me_2PhAs , $[\text{Fe}(\text{Ph}_2\text{As} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{AsPh}_2)\{\text{S}_2\text{C}_2(\text{p-MeC}_6\text{H}_4)_2\}]^0$,
 $[\text{Ni}\{\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2\}\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]^0$ and $[\text{M}\{\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2\{\text{S}_2\text{C}_2(\text{CN})_2\}]^0$
($\text{M} = \text{Fe}$ or Co) have also been prepared and studied. It has been shown
that the species $[\text{M}(\text{L})(\text{S-S})_2]^-$, where $\text{L} = \text{o-C}_6\text{H}_4(\text{AsMe}_2)_2$,
 $\text{Ph}_2\text{AsCH}_2 \cdot \text{CH}_2 \cdot \text{AsPh}_2$ and cis- $\text{Ph}_2\text{P} \cdot \text{CH} : \text{CH} \cdot \text{PPh}_2$, are six-coordinated,
whereas the species $[\text{M}(\text{L})(\text{S-S})_2]^0$, where $\text{L} = \text{Ph}_2\text{As} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{AsPh}_2$ are

five coordinated. In similar studies²²⁷ with iron and cobalt complexes, J.A. McCleverty et al. have given the possibility that the species $\left[M(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{S}_2\text{C}_2\text{R}_2)_2 \right]^Z$ ($M = \text{Fe}$ or Co) might be six coordinate. The diphosphine behaved as bidentate in these complexes when $Z = -1$ and $R = \text{CN}$ or CF_3 , and as monodentate when $Z = 0$ and $R = \text{aryl group}$.

Bridged binuclear bis-dithiolene complexes of iron and cobalt have also appeared in literature.²²⁸ G.E. Eaton and coworkers²²⁸ prepared the complexes $\left[(\text{R}_4\text{C}_4\text{S}_4)_2 \text{M}-(\text{L-L})-\text{M}(\text{S}_4\text{C}_4\text{R}_4) \right]^Z$ with $Z = 2^-$, $R = \text{CN}$, CF_3 and $Z = 0$, $R = \text{CF}_3$, $(\text{L-L}) = 1,4\text{-bis(diphenylphosphino)-benzene}$, $\text{bis(diphenylphosphino)acetylene}$, or trans-1,2-bis(diphenylphosphino)ethylene and studied their magnetic moment, electronic spectra, e.p.r. and polarograph. Magnetic moment of these complexes indicate them to be five coordinate species and polarographic measurements reveal a three member electron transfer series ($Z = 2^-$, 1^- , 0), (L-L) being a bidentate bridging ligand.

Mössbauer spectra of tetrabutylammonium salt of bis(maleonitriledithiolato)iron(III), tris-tetraphenylphosphonium tris(1,2-dicyanoethylene-1,2-dithiolene)iron(III) and electron paramagnetic resonance spectra of a number of ferric complexes have been investigated.²²⁹⁻²³¹

Kinetic investigations on the reactions of iron(III) and iron(IV) dithiolato complexes with organic bases indicate²³² that the five coordinated complexes and their six-coordinate analogues

with bidentate bases are labile. Equilibrium constant and rate of the reaction have also been measured. The substitution reactions of cobalt dithiolene system²³³ indicate a transformation of six coordinate adduct to a five-coordinate adduct.

Single crystal X-ray studies²³⁴ reveals that palladium and platinum bis(ethylene-1,2-dithiolene) complexes contain metal-metal bonds in their structures and the molecular structure of $MS_4C_4H_4$ ($M = Pd, Pt$) complexes, consists of two essentially planar, $MS_4C_4H_4$ units joined by a direct metal-metal bond.

Recently²¹⁸ it is found that metal-dithiolene complexes and related compounds react analogously to substitute ethylene system with regard to the redox behaviour (one-electron transition formation of radical anion). Behaviour and application of various types of dithiolene and metal-dithiolene are also discussed.²³⁵

Voltammetric studies show that the complex²³⁶ $[Re\{S_2C_2(CN)\}_2]_2^{-2}$ should have the formula,²³⁷ $[Re\{S_2C_2(CN)\}_2]_4^{-4}$.

Copper(II) complexes of dithiooxalate have been prepared.²³⁸ The i.r., magnetic moment and voltammetry have been studied. By analogy to other complexes, the complex $[Cu(L)_2]^{-2}$ has a planar structure

It has been observed²³⁹ that triphenylphosphine-oxide, triphenylarsine oxide, pyridine N-oxide and halide ions convert the dimers $[Fe_2S_8C_8R_8]^{-2}$ ($R = CN, CF_3$) into monomers and give adducts of the type (base) $(FeS_4C_4R_4)^-$. The i.r., magnetic moments and electronic

spectra of these adducts have been studied.

Mixed dithiolene and carbonyl complexes have also been prepared. C.J. Jones and coworkers²⁴⁰ prepared $(\text{CF}_3)_4\text{C}_4\text{S}_4\text{Fe}(\text{CO})_3$ and suggested a dimeric, sulphur bridged structure for the complex on the basis of solution molecular weight. J. Miller and A.L. Balch²⁴¹ have shown that this complex should have the formula $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Fe}(\text{CO})_3$. The latter formulation is supported by mass and i.r. spectral data. Bis(perfluoromethyl)dithietene reacts with triruthenium dodecacarbonyl at 100°C , to give an orange carbonyl containing complex $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Ru}_2(\text{CO})_6$ (a polymer) and at higher temperature (170°C) a green carbonyl free complex. Reaction of the orange material with group V bases yield species of the type $(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Ru}(\text{CO})_n(\text{ER}_3)_{3-n}$. With triphenylphosphine, two different solid complexes (orange and violet) having the composition $[(\text{CF}_3)_2\text{C}_2\text{S}_2\text{Ru}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$ have been obtained. These two species are structural isomer. X-ray studies on violet form predict to have the square-pyramidal configuration. The green coloured complex reacts with group V bases to yield $(\text{base})[\text{RuS}_4\text{C}_4(\text{CF}_3)_4]$ and $(\text{base})_2[\text{RuS}_4\text{C}_4(\text{CF}_3)_4]$ $(\text{base}) = (\text{C}_6\text{H}_5)_3\text{P}$, $(\text{C}_6\text{H}_5)_3\text{As}$ and $(\text{C}_6\text{H}_5)_3\text{Sb}$. The monoadducts are square pyramid whereas bisadducts are probably pseudo-octahedral.

1,1- and 1,2-Dithiolato ligand systems have also been examined. Nickel bis-complexes with two different 1,2-dithiolato ligands were reported²⁴² and the exchange reactions of these and related 1,2-dithiolene

were studied with voltammetric techniques.^{242,243}

Tris complexes with mixed 1,1- and 1,2-dithiolene ligands were also prepared and investigated recently.^{244,245}

Recently R.H. Holm and coworkers^{246,244} reported the synthesis and stereochemical investigations of unusual complexes viz., bis(N,N-disubstituted dithiocarbamato)-1,2-bis(perfluoromethyldithiolene)iron $\text{Fe}(\text{R}_1\text{R}_2\text{dtc})_2\text{tfd}$ and they have shown that compounds with $\text{R}_1\text{R}_2 = \text{Me}, \text{Me}; \text{Et}, \text{Et}; \text{Me}, \text{Ph}; (\text{CH}_2)_4; (\text{CH}_2)_5$ display following three properties in the same molecular species (i) magnetic behaviour consistent with a singlet-triplet spin equilibrium in the solid and solution phase; (ii) redox properties indicative of a three-membered electron transfer series; (iii) stereochemical non-rigidity of a ligand structural portion (restricted rotation about $\text{S}_2\text{C}-\text{N}$ bond) and of the overall molecular configuration itself (inversion). The X-ray results have shown²⁴⁷ that $\text{Fe}-\text{S}_6$ coordination unit assumes a stereochemistry intermediate between idealized octahedral and trigonal prismatic geometry.

The magnetic moment, kinetic and NMR studies²⁴⁸ have been performed on several complexes of bis(N,N-disubstituted dithiocarbomato)-(maleonitriledithiolene)iron complexes $\text{Fe}(\text{R}_1\text{R}_2\text{dtc})_2\text{mnt}$, ($\text{R}_1\text{R}_2 = \text{Et}, \text{Et}$ or Me, Ph).

Voltammetric studies²⁴⁹ in dichloromethane indicated that the mixed complexes of 1,1/1,2-dithiolene $\text{M}[\text{S}_2\text{C}_2(\text{CN})_2][\text{S}_2\text{CNR}_2]^Z$ with

$Z = -1$, $M = \text{Ni, Cu, Pd, Pt}$ and with $Z = 0$, $M = \text{Ni, Cu, Au}$,

$M[\text{S}_2\text{C}_2(\text{CN})_2][\text{S}_2\text{CNCN}]^{-2}$ $M = \text{Ni, Pd}$ and $\text{Ni} [\text{S}_2\text{C}_2(\text{CN})_2][\text{S}_2\text{COC}_2\text{H}_5]^{-}$

could be oxidized in a one electron step.

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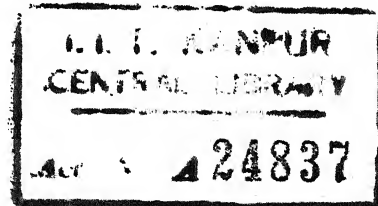
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S E C T I O N - A

CHAPTER II

CHELATING BEHAVIOUR OF 2,4-DITHIOURACIL-I*

(Co(II), Ni(II), Cu(II), Cd(II),
Pb(II), Ag(I), Tl(I) and Au(III))

In this chapter, the preparations, the magnetic and the spectroscopic (infrared and visible) studies of 2,4-dithiouracil complexes with cobalt(II), nickel(II), copper(II), cadmium(II), lead(II), silver(I), thallium(I) and gold(III) are reported. From these studies the structures of the complexes have been proposed.

EXPERIMENTAL

All reagents used were of Analar or chemically pure grade.

(A) Preparation of 2,4-Dithiouracil

2,4-Dithiouracil, $C_4H_4N_2S_2$ (hereafter referred to as TU), was prepared by the method given in the literature.¹ The ligand was recrystallized from boiling water before use. The compound analysed correctly to $C_4H_4N_2S_2$.

* Indian Journal of Chemistry, 10, 652-656 (1972).

(B) Preparation of Metal-Complexes

(a) Nona-(2,4-dithiouracil)diaquatetracobaltete(II).— One hundred ml of a solution containing about 6 mmole of the ligand (TU) in hot *n*-butanol was mixed slowly with 100ml solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ containing ~ 2 mmole in hot *n*-butanol. The mixture was digested for about four hours on the water bath. A precipitate appeared which was filtered out, washed successively with hot *n*-butanol, water and ethanol to remove all the unreacted Co^{++} ion and the ligand. It was dried in an air oven at 120°C for about eight hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Co}_4(\text{TU})_9(\text{H}_2\text{O})_2$: C, 27.6; H, 2.0; N, 16.0; S, 36.7; Co, 15.0. Found: C, 27.8; H, 1.9; N, 15.8; S, 37.1; Co, 14.5.

(b) Mono(2,4-dithiouracil)dipyridine nickel(II).— To a solution of 0.4 g (~ 1.5 mmole) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 50 ml water, a few ml of pyridine was added in order to get a deep-blue solution of nickel-pyridine complex. To this, a solution of 0.3 g (~ 2 mmole) of the ligand in 50 ml of ethanol was added slowly whereupon a greenish blue precipitate appeared. It was digested for half an hour on a water bath. The precipitate of the complex was centrifuged and washed successively with water and ethanol. It was dried in a vacuum desiccator at room temperature for a few days, yielding a greenish blue coloured complex.

Anal. Calcd. for $\text{Ni}(\text{TU})\text{Py}_2$: C, 46.6; H, 3.6; N, 15.5; S, 17.8; Ni, 16.4. Found: C, 46.8; H, 3.6; N, 15.3; S, 17.5; Ni, 16.1.

(c) Bis(2,4-dithiouracil)copper(II).— 0.6 g sample of the ligand (~ 4 mmole) and 0.8 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (~ 4 mmole) were dissolved separately in 100 ml and 50 ml respectively of ethanol. The two solutions were mixed which resulted in a reddish precipitate. On digesting over a water bath for about twelve hours, the red coloured precipitate changed to yellow. The precipitated complex was filtered out, washed successively with hot water and ethanol. It was dried overnight in an air oven at 120°C , yielding a yellow complex.

Anal. Calcd. for $\text{Cu}(\text{TU})_2$: C, 27.5; H, 1.7; N, 16.0; S, 36.6; Cu, 18.1. Found: C, 26.9; H, 1.5; N, 16.4; S, 36.4; Cu, 18.2.

(d) Bis(2,4-dithiouracil)tetraaquo nickel(II).— 0.5 g sample of the ligand (~ 3.4 mmole) and 0.5 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (~ 1.7 mmole) were dissolved in 60 ml and 100 ml respectively of boiling acetone. The two solutions were mixed and digested for about forty five minutes on a water bath. The precipitate of the yellow complex was filtered out and washed successively with hot water and acetone. It was dried in an air oven at 120°C for a few hours, yielding a yellow coloured complex.

Anal. Calcd. for $\text{Ni}(\text{TU})_2(\text{H}_2\text{O})_4$: C, 23.0; H, 2.4; N, 13.4; S, 30.7; Ni, 14.2. Found: C, 23.6; H, 1.73; N, 13.9; S, 30.3; Ni, 14.2.

(e) Mono(2,4-dithiouracil)cadmium(II).— 0.4 g sample of the ligand (~ 2.7 mmole) was dissolved in 50 ml of boiling acetone. Another

solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was prepared by dissolving 0.9 g of the cadmium nitrate (~ 2.8 mmole) in 25 ml of acetone at room temperature. The two solutions were mixed whereby a cream coloured precipitate appeared. It was digested on a water bath for about three hours. The precipitated complex was filtered out and washed several times with hot acetone. It was dried in an air oven at 120°C for a few hours, yielding a cream-coloured complex.

Anal. Calcd. for $\text{Cd}(\text{TU})$: C, 18.7; H, 1.17; N, 10.9; S, 25.0; Cd, 43.8. Found: C, 18.5; H, 1.36; N, 10.9; S, 24.3; Cd, 43.9.

(f) Mono(2,4-dithiouracil)lead(II).— Two solutions of the ligand and lead acetate were prepared by dissolving a 0.3 g sample of the ligand (~ 2 mmole) in 50 ml of ethanol and 0.8 g of $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ (~ 2.1 mmole) in 80 ml of methanol respectively. These were mixed resulting in a light yellow coloured precipitate. It was kept overnight at room temperature and centrifuged. The precipitate was washed successively with hot methanol, ethanol and finally with ether. It was dried in a vacuum desiccator at room temperature for a few days, yielding a light yellow coloured complex.

Anal. Calcd. for $\text{Pb}(\text{TU})$: C, 13.6; H, 0.66; N, 7.1; S, 18.2; Pb, 60.4. Found: C, 13.7; H, 0.57; N, 7.2; S, 18.2; Pb, 59.9.

(g) Mono(2,4-dithiouracil)disilver(I).— 0.3 g sample of the ligand (TU) (~ 2 mmole) and 0.7 g of AgNO_3 (~ 4.1 mmole) were dissolved

respectively in 50 ml ethanol and 50 ml of distilled water. The two solutions were mixed whereupon a yellow precipitate appeared. It was digested for about half an hour on a water bath. The precipitated complex was filtered out and washed successively with hot distilled water and ethanol. It was dried in an air oven at 120°C for a few hours, yielding a yellow complex.

Anal. Calcd. for $\text{Ag}_2(\text{TU})$: C, 13.3; H, 1.11; N, 7.8; S, 17.8; Ag, 60.0. Found: C, 13.1; H, 0.8; N, 7.6; S, 17.5; Ag, 59.2.

(h) Tris(2,4-dithiouracil)digold(III).— 0.4 g sample of the ligand (~ 2.7 mmole) was dissolved in 70 ml of ethanol and 0.6 g (~1.9 mmole) of AuCl_3 , in 50% ethanol. The two solutions were mixed, whereupon a buff coloured precipitate appeared. On digesting over a water bath for about forty five minutes, the colour of the precipitate changed to yellow. The precipitate of the complex was filtered out and washed successively with hot distilled water and ethanol. It was dried in an air oven at 120°C, yielding a yellow complex.

Anal. Calcd. for $\text{Au}_2(\text{TU})_3$: C, 17.4; H, 1.45; N, 10.2; S, 23.2; Au, 47.7. Found: C, 17.6; H, 1.83; N, 9.9; S, 23.3; Au, 47.9.

(i) Mono(2,4-dithiouracil)diaquothallium(I).— 0.3 g sample of the ligand (~ 2 mmole) was dissolved in 50 ml of ethanol and 0.5 g of TlNO_3 (~1.8 mmole) in boiling water. On mixing the two solutions, a yellow precipitate appeared. It was digested for about half an hour on a water bath. The precipitated complex was separated by filtration

and washed successively with boiling water and ethanol. It was dried in an air oven at 120°C overnight, yielding a bright yellow coloured complex.

Anal. Calcd. for $\text{Tl}(\text{TU})(\text{H}_2\text{O})_2$: C, 12.6; H, 1.57; N, 7.1; S, 16.7; Tl, 53.4. Found: C, 12.7; H, 1.76; N, 7.4; S, 16.0; Tl, 54.0.

Analyses

The analyses of the metal ions and sulphur were carried out by the standard methods.^{2,3} Carbon, hydrogen, and nitrogen analyses were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur, India. The analytical results are given in the text.

Infrared Spectra.— Infrared spectra of the ligand and the metal complexes were recorded with a Perkin-Elmer 521 Diffraction grating Infrared Spectrophotometer in the 4000–250 cm^{-1} range. Samples were prepared as potassium bromide pellets. The major bands of the infrared spectra of the ligand and the complexes are given in Table I.

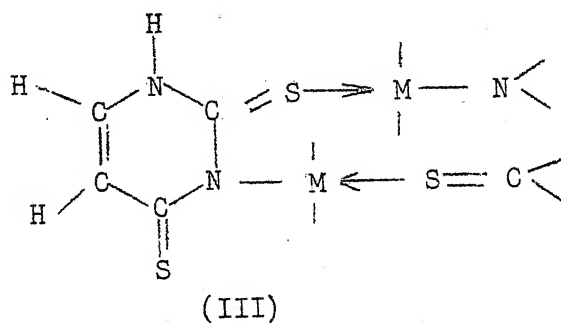
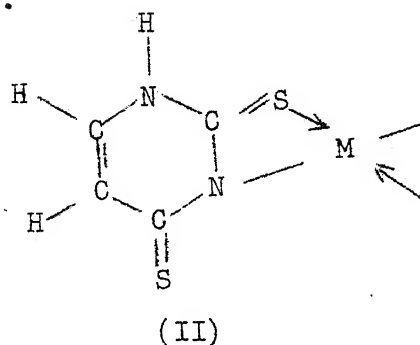
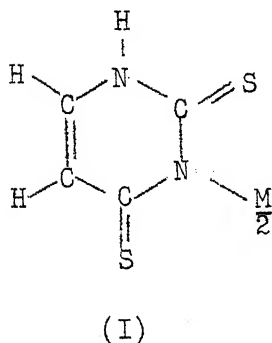
Magnetic Susceptibility Measurements.— The magnetic susceptibilities of the complexes were determined with the help of a Gouy-balance at room temperature (27°C). Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard and the diamagnetic corrections were estimated by a method outlined by Figgis and Lewis.⁴ The results are given in Table II.

UV and Visible Spectra.— The absorption spectra of the ligand and the complexes were recorded on a Cary-14 recording Spectrophotometer in nujol mull between 300 and 1500 m μ . The results are given in Table II.

RESULTS AND DISCUSSION

The analytical data suggest that the ligand is acting as mono-, bi-, tri-, or tetradentate in the formation of the complexes. Comparing the stoichiometries with the known preferences of all the metal ions of for a coordination number/four or six, it would appear rather certain that in cadmium, lead and nickel-pyridine complexes, the ligand acts as tetradentate, in copper complex as tridentate, in cobalt and thallium complexes as bidentate, and in silver and nickel-aquo complexes as monodentate. In cases where the ligand is tetradentate, coordination of the metal ion is assumed to be through all the nitrogen and thio-carbonyl sulphur atoms. As a tridentate, the ligand is assumed to coordinate through two thiocarbonyl sulphur atoms and one of the nitrogen atoms. When the ligand is behaving as bidentate, the metal ion can form either a simple salt(I) by linking with one of the nitrogen atoms or an inner complex (II) or a polymer (III) by forming bonds with nitrogen and sulphur atoms. (It is possible that the ligand in solution can exist as thiol due to thiol-thione tautomerism in which case, the complexes should be formed by replacing the protons of the thiol group with the metal ion. However, the thione form of the ligand⁵ has been used here, whereby a coordinate bond is formed by donating a

lone pair of electrons of the thiocarbonyl sulphur to the metal atom). In the structures I, II and III, the coordination utilizing 2,3-positions have been shown. However, coordination utilizing 1,2- or 3,4-positions may also take place.



The infrared spectra of the complexes were studied in some detail and compared to that of the ligand spectrum. It might give some information about the surroundings around metal ions. The positions of main infrared bands of the complexes and those of the ligand are given in Table I. Since the thioamide groups were believed to be involved in coordination with the metal ions, the major shifts are expected in the positions of the bands arising, owing to the stretching of the bonds and the bending of the angles of the two H-N-C-S groups of the ligand. Such major shifts along with the discussion are summarized below:

(a) The band in the spectrum of the ligand around 3000 cm^{-1} is a very broad one, which is much less broad in the spectra of the complexes. This broadening may be attributed⁶ to the associated N-H groups of the ligand. However, four intense and more or less sharp bands are present in the spectrum of the ligand at 3220 cm^{-1} , 3165 cm^{-1} , 3070 cm^{-1} and 2880 cm^{-1} . These bands are assigned⁷ to the coupled vibrational normal modes arising due to ν (C-H) and ν (N-H). These fundamental bands disappear and the new medium intense, not very sharp bands appear at 2920 cm^{-1} and 3060 cm^{-1} in spectra of the silver, cadmium, nickel-pyridine and lead complexes, at 2920 cm^{-1} , 3060 cm^{-1} and 3140 cm^{-1} in the spectra of other complexes. The bands around 2920 cm^{-1} , 3060 cm^{-1} in the lead and silver complexes are assigned to ν_{as} (C-H) and ν_s (C-H) of $\text{HC}=\text{CH}$ part of the ligand. The new third band around 3140 cm^{-1} in other cases may be explained on the assumption that in the complexes only one of the N-H group is deprotonated with the formation of nitrogen to metal bond and thereby one single band due to ν (N-H) appears in their spectra. However, it is quite possible that this band may not be a pure one but may arise due to the normal coordinate having some contribution from ν (C-H). Similarly the bands around 2920 cm^{-1} and 3060 cm^{-1} may have some contribution from ν (N-H). The band around 3140 cm^{-1} is not as broad as that in the pure ligand. This may be due to the lesser intramolecular interaction in the complexes as compared to that in the ligand.

(b) In the ligand the two H-N-C-S groups are adjacent to each other and it would be rather certain that the four characteristic

thioamide bands^{8,9} will be either broad or split ones due to the strong interaction between their vibrational modes. Also owing to the close proximity of (C=C) and (C-H) groups, the thioamide bands may be coupled with ν (C=C) and δ (C-H). The frequencies corresponding to these bands are given in Table I. (It will be interesting to point out that the previous workers¹⁰ have assigned bands around 1100 cm^{-1} to ν (C=S) in the spectra of the ligand which appears to be rather high for ν (C=S) in such a highly delocalized system.^{11,12} The frequencies arising due to normal coordinates having contributions from ν (C=S) are given in Table I. It is obvious from the data that all the thioamide bands are shifted in the spectra of the complexes indicating a different interaction of the two thioamide groups in the complexes from the interaction in the of those ligand. Assuming the deprotonation of one or both of the N-H groups and the coordination of the metal ion with nitrogen and sulphur as mentioned in the foregoing paragraphs, the assignments of the shifted bands are given in Table I. It appears that the thioamide band IV at 780 cm^{-1} and 795 cm^{-1} in the ligand having major contribution from ν (C=S) are shifted to higher frequency ($\sim 820\text{ cm}^{-1}$) in the complexes. There is another very weak band at 600 cm^{-1} which may also be assigned to the normal coordinate having major contribution from coordinated ν (C=S). It is also suggested that the band around 820 cm^{-1} contains major contribution of the uncoordinated ν (C=S) mode.

(c) The bands at 400 cm^{-1} , 445 cm^{-1} , 465 cm^{-1} , and 985 cm^{-1} are assigned to the skeletal vibration of the pyrimidine ring.⁵ In

the complexes the positions of these bands are only a little shifted ($\sim 10 \text{ cm}^{-1}$).

(d) In the spectrum of the nickel complex containing pyridine, most of the pyridine bands shift after complexation indicating an interaction of pyridine with the metal ion.

(e) In the region $300 \text{ cm}^{-1} - 425 \text{ cm}^{-1}$ two new but somewhat broad and less intense bands appear in the spectra of all the complexes. These bands can not be due to either pure ν (M-S) or ν (M-N) modes of vibrations. Both these bands must be having contributions from ν (M-S) and ν (M-N). Besides these must also be having some contribution from bending or skeletal modes of vibration of the pyrimidine ring. Therefore, these bands are assigned^{13,14} to the normal modes having major contribution from ν (M-N) and ν (M-S).

(f) The absence of weak band in the region of 2600 cm^{-1} in the spectrum of the ligand and those of the complexes, suggest that the ligand in the complexes are present in the thione form and not in the thiol form.

(g) In the spectra of the cobalt and thallium complexes, a broad band around 3300 cm^{-1} is found, which is assigned to ν (O-H) of coordinated water.

The preceding discussion of the infrared spectra and chemical analyses of the complexes indicates: (i) that in cadmium, nickel, and lead complexes, the ligand is acting as tetradentate,

in copper complex, as tridentate, in cobalt and thallium complexes, as bidentate, in $\text{Ni}(\text{TU})_2(\text{H}_2\text{O})_4$ and silver complexes, as monodentate; (ii) that the bonding with the metal ion in the complexes except silver complex and $\text{Ni}(\text{H}_2\text{O})_4(\text{TU})_2$ are through thiocarbonyl sulphur and nitrogen of the deprotonated N-H group, thus forming an inner complex type of structure (II) and not the salt type (I). It is hard to distinguish between the inner complex structure (II) and polymeric structure (III). However, the polymeric type of structure (III) is preferred over the inner structure (II) owing to complete insolubility of all the complexes in most of the organic and inorganic solvents (Table II). In $\text{Ni}(\text{TU})_2(\text{H}_2\text{O})_4$ and Ag_2TU both the N-H groups are deprotonated and the bonding may be through nitrogen only.

Visible Spectra and Magnetic Properties

The magnetic and the visible-spectral properties of the complexes were studied to understand the spatial arrangements of the ligand around the metal ions.

All the complexes are diamagnetic except cobalt(II), nickel-pyridine, nickel-aqua, and copper complexes, whose observed values of corrected magnetic moments at room temperature are 1.4 B.M., 2.8 B.M., 2.2 B.M. and 1.8 B.M., respectively.

The visible spectrum of the ligand in nujol mull exhibits two moderately intense bands at $26,670\text{ cm}^{-1}$ and $28,570\text{ cm}^{-1}$. These bands are assigned to $n \rightarrow \pi^*$ transitions of the thiocarbonyl groups.

The splitting of the band may be due to the interaction of the two thiocarbonyl groups.

The spectrum of the nickel pyridine complex Ni(TU)Py_2 in nujol mull shows three broad and weak absorption bands ($10,000\text{ cm}^{-1}$, $14,700\text{ cm}^{-1}$, $22,730\text{ cm}^{-1}$). The positions of these bands are characteristic of those found for octahedral complexes of bivalent nickel. This suggests the octahedral surrounding of the ligand around nickel ion. Besides these three bands, there are two other moderately intense bands at $17,100\text{ cm}^{-1}$ and $27,000\text{ cm}^{-1}$ which may tentatively be assigned to the charge transfer bands in the complexes. $17,100\text{ cm}^{-1}$ band is not assigned to d-d transition because of its intensity. (Also if the crystal field parameters (B' , β , Dq) are calculated using this band as d-d transition, the calculated values are absurd). Since the symmetry of the field around nickel ion in the complex can never be O_h and a departure from O_h field towards that of lower symmetry should split up¹⁵ this band, any splitting which may be there in these bands due to lower symmetry is not resolved. However, 10000 cm^{-1} and $14,700\text{ cm}^{-1}$ bands are not symmetrical towards the high and low frequency sides respectively. From the positions of these three bands, the values of Dq , B' and β were calculated to be 1000 cm^{-1} , 495 cm^{-1} and 0.48 respectively. It may be noted that the values of B' and β are very low which is in accordance with the results obtained by Schaffer¹⁶ and Jørgensen¹⁷ who pointed out that the ligands coordinating through sulphur atoms frequently show low values of B' and β .

These low values further indicate that in the complex, thiocarbonyl sulphur is coordinating to the metal ion. This puts the ligand 2,4-di-thiouracil towards the strong end of the nephelauxetic series. The value of magnetic moment (2.8 B.M.) with practically no orbital contribution to the magnetic moment also independently demonstrates the octahedral symmetry around the nickel ion.¹⁸⁻²⁰

In nickel-aqua complex the magnetic moment is 2.2 B.M. This value is intermediate between that of the complex in the low spin state (0.5 B.M. due to residual paramagnetism) and in the high spin state (~ 3.2 B.M.). This indicates that the energy difference between the singlet and the triplet state has become comparable with the thermal energy. This may possibly be due to the lowering of the field along the z-axis below and above the metal ion which is bound to four donor atoms in the plane.²¹ (As the field along the z-axis decreases, singlet state which lies much above the triplet state in the octahedral complexes drops in relative energy. Thus depending upon the relative axial (along z-axis) field strength with respect to in plane field (along x- and y-axes) strength, the singlet-triplet states lie close together allowing a partial thermal transition and thus lowering the magnetic moment value).

The nujol mull spectrum of the nickel-aqua complex shows one unsymmetrical very broad band at 9075 cm^{-1} with a shoulder at $12,120\text{ cm}^{-1}$. It exhibits another shoulder at $14,300\text{ cm}^{-1}$. After $14,300\text{ cm}^{-1}$ there is a continuous strong absorption band with a maximum at $33,000\text{ cm}^{-1}$.

The bands at 9075 cm^{-1} and $14,300\text{ cm}^{-1}$ indicate an octahedral environment around nickel, and unsymmetrical nature of the band at 9075 cm^{-1} with a shoulder at $12,120\text{ cm}^{-1}$ suggests that the field around nickel ion is not of O_h type but of lower symmetry, possibly D_{4h} . (There is a possibility¹⁵ of the band at $12,120\text{ cm}^{-1}$ arising from the ${}^3A_2(F) \rightarrow {}^1T_2(D)$ transition. However, the author prefers that this band is due to departure from O_h symmetry towards D_{4h} . This is obvious from the magnetic data as well as from the intensity of this band which is nearly the same as that of 9095 cm^{-1} . If this would have been due to triplet \rightarrow singlet transition, the intensity should be very much less than that of a triplet \rightarrow triplet transition). The amount of splitting in the first band (${}^3A_{2g} \rightarrow {}^3T_{2g}$) is a measure $(35/4 Dt)$ of degree of distortion.¹⁵ Assuming D_{4h} symmetry the values of $Dq(xy)$ (907 cm^{-1}), Dt (348 cm^{-1}) and Dq^z (300 cm^{-1}) were calculated from the positions of these bands. The field along the z-axis is much smaller than that along the xy plane. This corresponds very well to the value of the magnetic moment of the complex. Thus, on the basis of i.r., visible spectral and the magnetic moments, structures IV and V are preposed for the nickel complexes.

The stoichiometry of the copper complex is $\text{Cu}(\text{TU})_2$. A simple oxidation reduction experiment shows the absence of copper in +1 oxidation state. Thus, one of the two N-H groups of the ligand is deprotonated. The value of the magnetic moment is 1.8 B.M. which falls in the range of octahedral complexes. The visible spectrum

shows a very broad band around $12,500\text{ cm}^{-1}$. Below $16,670\text{ cm}^{-1}$ there is a strong continuous absorption with a band around $28,570\text{ cm}^{-1}$ (ligand band). The unsymmetrical band around $12,500\text{ cm}^{-1}$ suggests²² the distorted octahedral structure of the copper complex. Thus, the insolubility of the complex in the organic and inorganic solvents, stoichiometry, paramagnetism corresponding to one unpaired electron and the visible, infrared spectra, suggest the structure VI for the copper complex. In this structure the ligand is behaving as a tridentate.

The spectrum of cobalt(II) complex, $\text{Co}_4(\text{TU})_9(\text{H}_2\text{O})_2$ shows five weak bands at $10,990\text{ cm}^{-1}$, $11,630\text{ cm}^{-1}$, $13,330\text{ cm}^{-1}$, $14,290\text{ cm}^{-1}$ and $15,150\text{ cm}^{-1}$ which presumably are d-d transitions. On the basis of these bands it is not possible to assign any definite structure of the complex. But it appears that the environment around the metal ion is not octahedral but there is a strong distortion from the octahedral symmetry. The value of the magnetic moment is also very low (less than that of one unpaired electron). From the magnetic moment value it appears that the ligands are arranged in a square-pyramidal structure (dsp^3) around cobalt ion and there is a spin-spin interaction which might arise due to direct cobalt-cobalt linkage of two square pyramidal units with the formation of σ -bond by the overlap of d_{z^2} orbitals.²³ (It is also possible that the low value of magnetic moment might possibly be due to the presence of cobalt in +3 oxidation state. However, it has been proved by simple oxidation reduction reactions that cobalt in

the complex is not present in +3 oxidation state). Its complete insolubility in organic and inorganic solvents indicate a polymeric structure. Thus, on the basis of the chemical analyses, infrared spectral, magnetic moment value, the structure VII is tentatively suggested for the complex. In the structure the ligand is acting as a bidentate.

Most of the cadmium(II), thallium(I) and lead(II) complexes mentioned in the literature are tetrahedral.²⁴ The complexes of these metal ions are diamagnetic. Therefore, the tetrahedral arrangement of the ligand molecule around Cd(II), Tl(I), and Pb(II) are assigned to these complexes. In cadmium and lead complexes the ligand is acting as tetradentate, while in others as bidentate.

The stoichiometry of silver and gold diamagnetic complexes are $\text{Ag}_2(\text{TU})$ and $\text{Au}_2(\text{TU})_3$ respectively. It is assumed that the complexes of silver(I) and gold(III) have salt like structures.

Table I

Assignments of Major Infrared Bands of the Ligand and the Complexes of Co(II), Ni(II), Cu(II), Pb(II), Cd(II), Tl(I), Ag(I) and Au(III)) (in cm^{-1})

Ligand	Complex	Assignments
-	3300	ν (OH) ^a
3220(s)	2920(b)	Coupled vibration due to ν (C-H) & ν (N-H) ^b . In Ag, Au, Pb complexes only ν (C-H).
3165(s)	3060	
3070(s)	3140(b)	
2880(b)		
1605(s, sh)	1600(m, sh)	δ (N-H) + ν (C=C), containing major contribution from ν (C=C)
1565(s, b)	1540	Thioamide band I ^c
1480(m, s, sh)	1500	
1410	1390	Skeletal vibration due to pyrimidine ring
1360	1320	
1210(s)	1190	Thioamide band II ^d
1230(s)	1200	
1250(s)	1220	
1128(s, sh)	1150	Thioamide band III ^e
1085(s, sh)	1100	
985(m)	985(w)	Characteristic vibrations of pyrimidine ring
860(s, sharp)	840	(C-H) out of plane vibration
780	820(b)	Thioamide band IV ^f
795	600(w)	
445	440	Characteristic bands of pyrimidine ring
465	465	
400	400	
-	300-425 (two broad medium intense bands)	ν (M-S) + ν (M-N) ^g

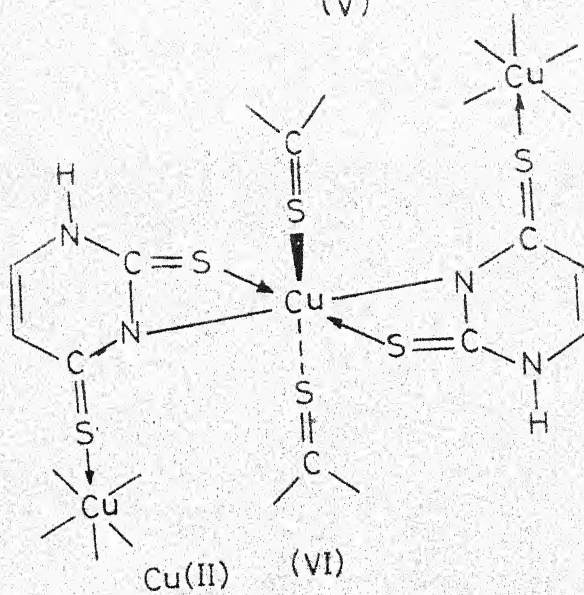
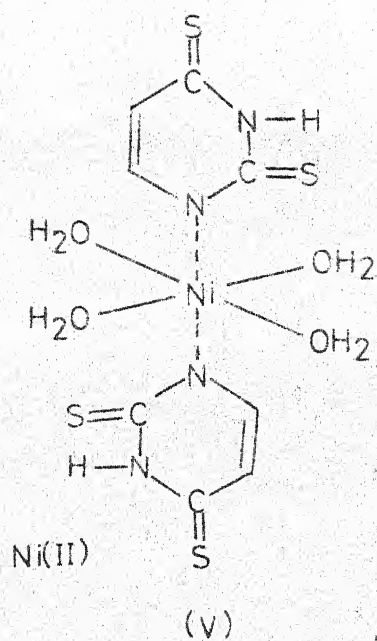
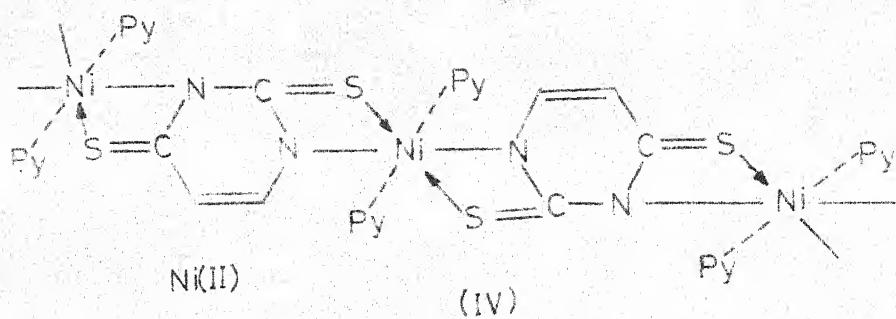
- a) These bands are present in the nickel-aqua and thallium complexes;
 b) 3140 cm^{-1} band is not present in the spectra of the silver, gold and lead complexes; c) due to δ (N-H) + ν (C-N) + ν (C=C); d) due to δ (N-H) + ν (C-N) + δ (C-H); e) mainly due to ν (C-N) + ν (C=S); f) mainly due to ν (C=S); g) the position of these bands vary with the metal ions.

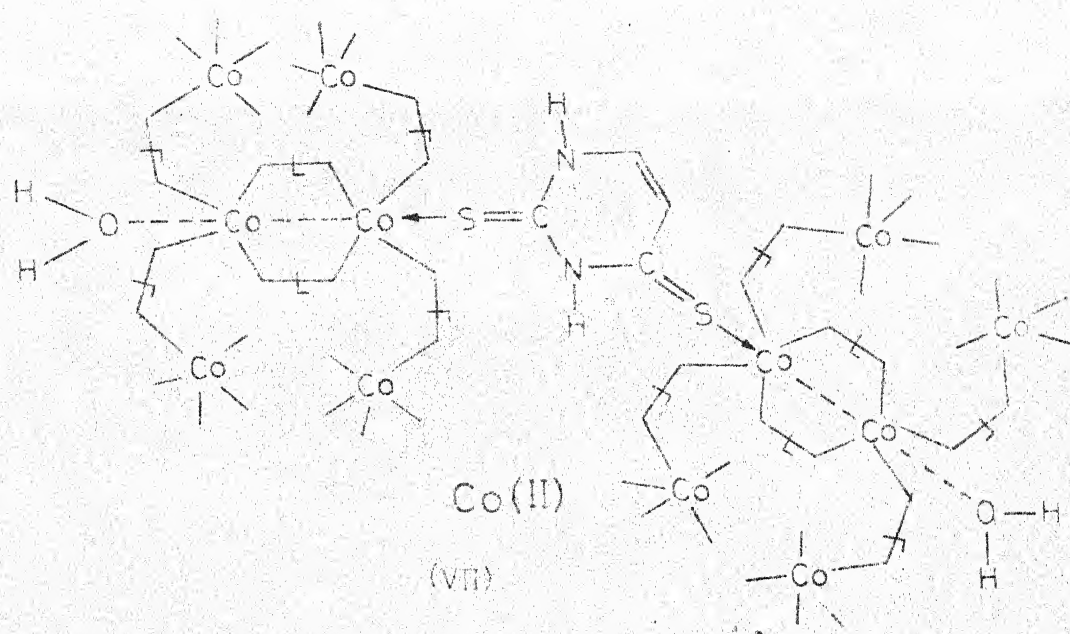
Table II

The Magnetic Moments, Solubilities, the Bands of the Electronic Spectra of the Complexes, and their Assignments

Complexes	$\mu^{\text{eff.}}$ B.M.	Solubi- lity	Position of the absorp- tion band (cm^{-1})	Assignments
$\text{Co}_4(\text{TU})_9(\text{H}_2\text{O})_2$	1.44	I	10,990 11,630 13,330 14,290 15,150	d-d transition
$\text{Ni}(\text{TU})\text{Py}_2$	2.8	I	10,000 14,700 22,730 17,100 27,000	$A_{2g} \rightarrow T_{2g}$ $A_{2g} \rightarrow T_{1g}(\text{F})$ $A_{2g} \rightarrow T_{1g}(\text{P})$ Charge transfer $n \rightarrow \pi^*$
$\text{Cu}(\text{TU})_2$	1.85	I	12,500 (unsymmetrical) 28,570	Characteristic of octahedral complex Ligand band
$\text{Ni}(\text{TU})_2(\text{H}_2\text{O})_4$	2.2	I	9,075 (unsymmetrical very broad) 12,120(sh) 14,300(sh)	${}^3B_{1g} \rightarrow {}^3E_g^a$ ${}^3B_{1g} \rightarrow {}^3B_{2g}$ ${}^3B_{1g} \rightarrow {}^3A_{2g}$
$\text{Cd}(\text{TU})$	D	I)		
$\text{Pb}(\text{TU})$	D	I)		
$\text{Ag}_2(\text{TU})$	D	I)		
$\text{Au}_2(\text{TU})_3$	D	I)		
$\text{Tl}(\text{TU})(\text{H}_2\text{O})_2$	D	I)		
				No d-d transition

D) Diamagnetic; I) Insoluble in chloroform, carbontetrachloride, benzene, tetrahydrofurane, cyclohexane, xylene, toluene, acetone, methanol, dioxane, dichloro-ethane and dichloro-methane.





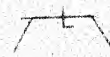
 = 2,4-Dithiouracil ligand acting as a bidentate by coordinating through nitrogen and thiocarbonyl sulfur atoms.

Fig. II.1

1. 2,4-Dithiouracil
2. $\text{Co}_4(\text{TU})_9(\text{H}_2\text{O})_2$
3. $\text{Ni}(\text{TU})\text{Py}_2$
4. $\text{Cu}(\text{TU})_2$
5. $\text{Ni}(\text{TU})_2(\text{H}_2\text{O})_4$
6. $\text{Cd}(\text{TU})$
7. $\text{Pb}(\text{TU})$
8. $\text{Ag}_2(\text{TU})$
9. $\text{Au}_2(\text{TU})_2$
10. $\text{Tl}(\text{TU})(\text{H}_2\text{O})_2$.

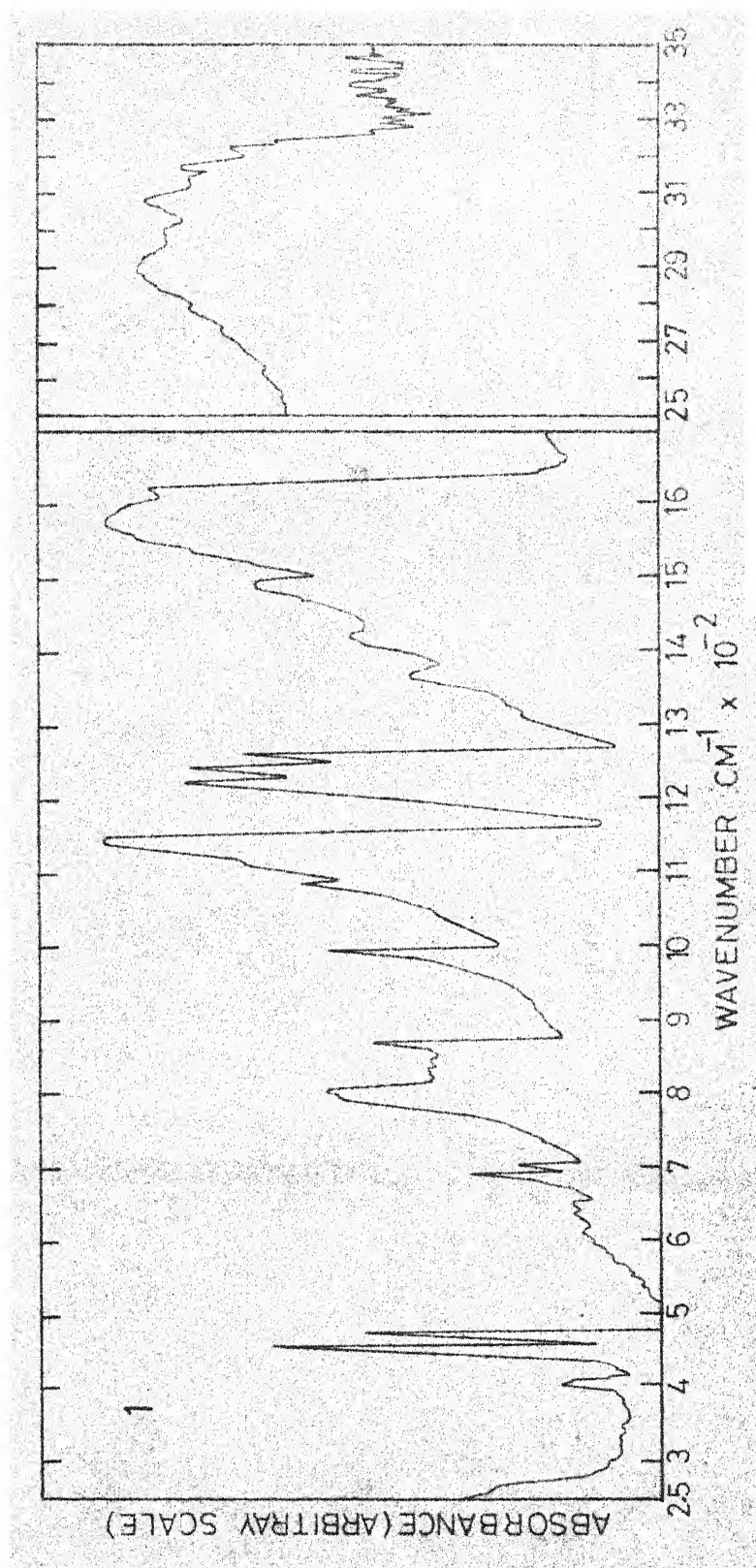


Fig.II.1

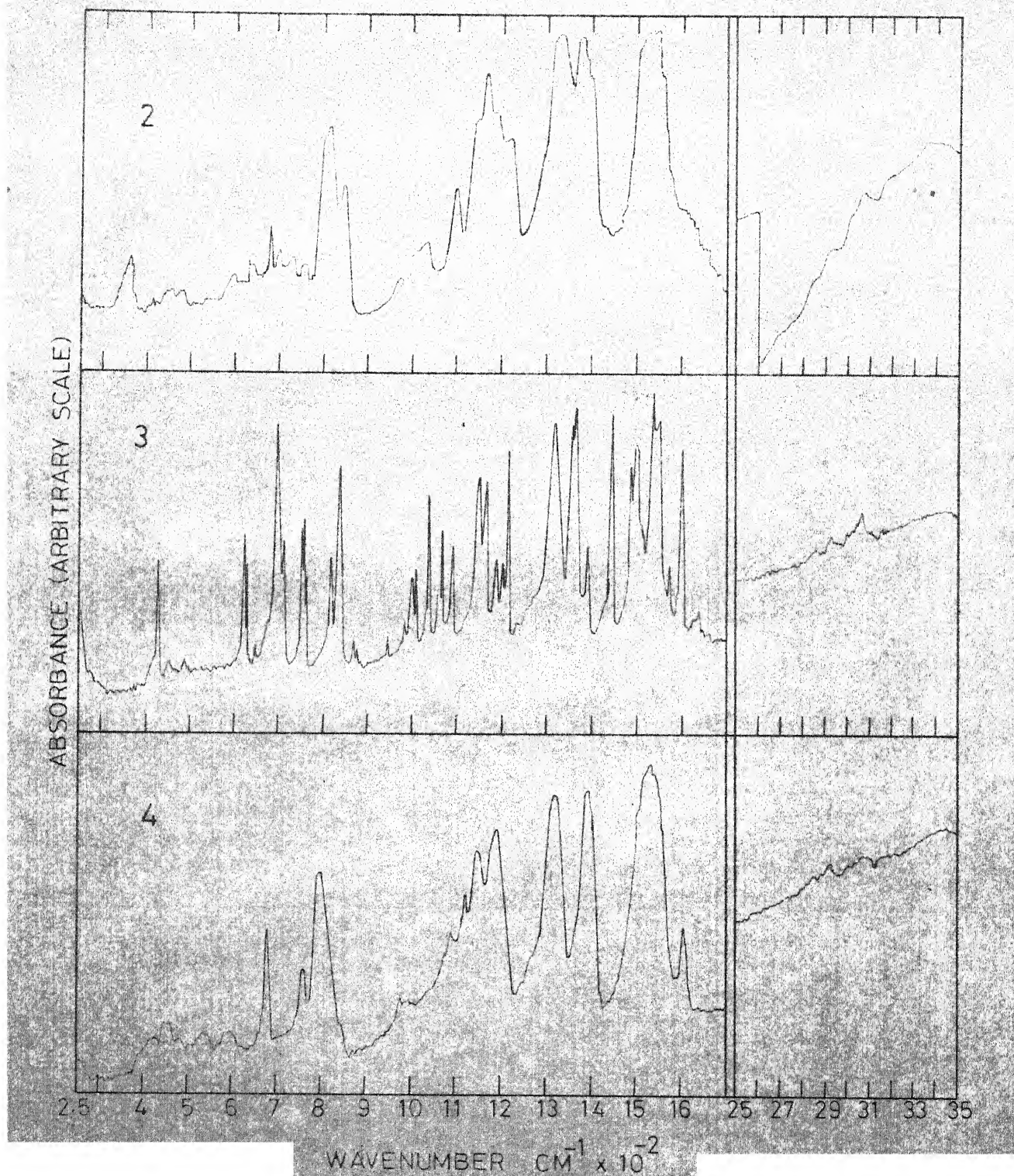


Fig. II.1

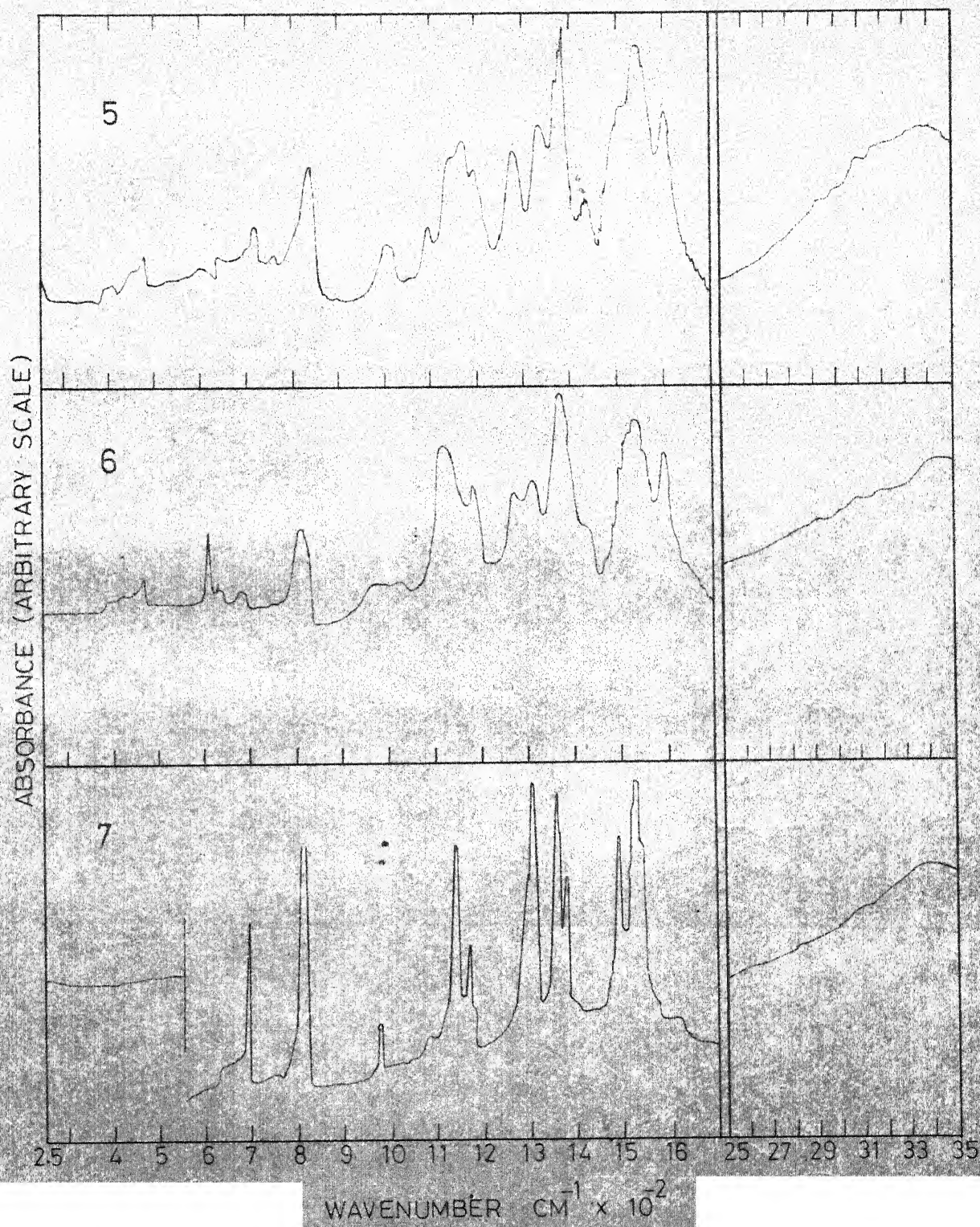


Fig. II.1

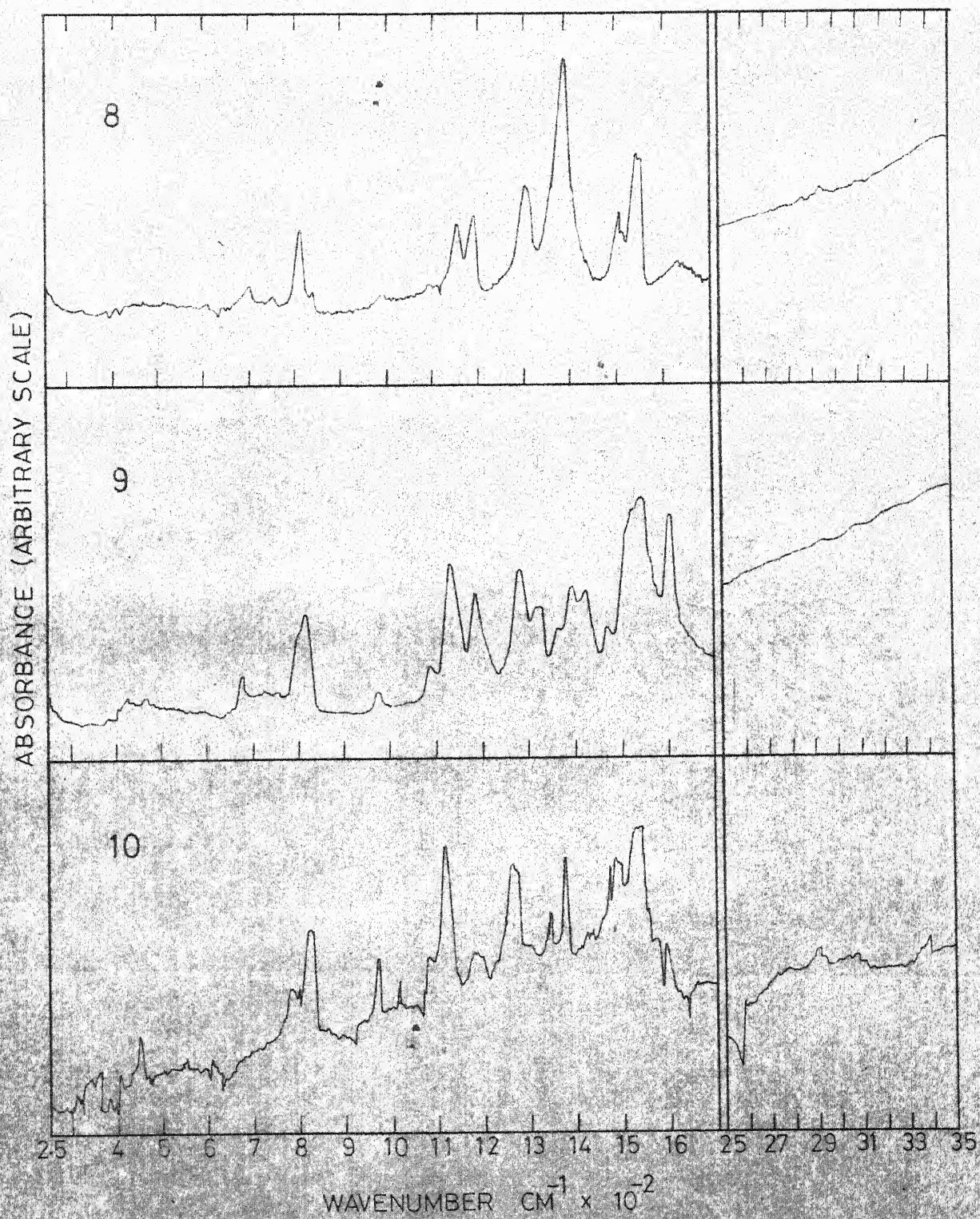


Fig. II.1

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CHAPTER III

CHELATING BEHAVIOUR OF 2,4-DITHIOURACIL-II*

(Rh(III), Ru(III), Pd(II),
Pd(IV), Pt(II) and Pt(IV))

In this chapter the preparations, structural aspects of the complexes of Rh(III), Ru(III), Pt(II), Pd(II), Pt(IV) and Pd(IV) have been reported.

EXPERIMENTAL

(A) Preparation of 2,4-Dithiouracil

2,4-Dithiouracil, $C_4H_4N_2S_2$ was prepared by the method given in Chapter II.

(B) Preparation of Metal Complexes

(a) Bis(2,4-dithiouracil)monochlororhodium(III).-- Fifty ml of the ligand solution in ethanol containing 0.3g (~ 2 mmole) and 100 ml of ethanolic solution of $RhCl_3$, having 0.21 g (~ 1 mmole) of the

* Indian Journal of Chemistry, 10, 657-659 (1972).

salt were mixed and digested on a water bath for six hours. On digestion a precipitate appeared, which was filtered out, washed successively with hot water and ethanol. It was dried in an air oven at 120°C for about six hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Rh}(\text{TU})_2\text{Cl}$: C, 22.5; H, 1.4; N, 13.1; S, 30.0; Rh, 24.1; Cl, 8.2. Found: C, 22.8; H, 1.6; N, 13.2; S, 29.8; Rh, 24.3; Cl, 7.9.

(b) Pentakis(2,4-dithiouracil)monochloro diruthenium(III).— 0.43 g sample of the ligand (~ 2.9 mmole) in 85 ml of ethanol and 0.31 g of the $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (~ 1.4 mmole) in 100 ml of ethanol were dissolved. The two solutions were mixed. The mixture was digested for about three hours on a water bath. The precipitate of the complex was filtered, washed successively with hot water and ethanol. It was dried in an air oven at 120°C for about eight hours, yielding a dark gray coloured complex.

Anal. Calcd. for $\text{Ru}_2(\text{TU})_5\text{Cl}$: C, 25.0; H, 1.6; N, 14.6; S, 33.4; Ru, 21.1; Cl, 3.7. Found: C, 24.8; H, 1.7; N, 14.2; S, 33.1; Ru, 20.7; Cl, 4.0.

(c) Bis(2,4-dithiouracil)palladium(II).— 0.57 g (~ 3.8 mmole) sample of the ligand was dissolved in 100 ml of ethanol and 0.35 g (~ 1.9 mmole) of the PdCl_2 , in boiling distilled water. The two solutions were mixed whereupon a yellowish brown coloured precipitate appeared. The precipitate was digested on a water bath for about five hours.

The precipitate of the complex was filtered, washed successively with hot water and ethanol. It was dried in an air oven at 120 °C for a few hours, yielding a yellowish brown complex.

Anal. Calcd. for $\text{Pd}(\text{TU})_2$: C, 24.4; H, 2.0; N, 14.2; S, 32.4; Pd, 26.8. Found: C, 24.1; H, 1.8; N, 13.9; S, 32.1; Pd, 26.5.

(d) Pentakis(2,4-dithiouracil)dichlorodipalladium(IV).— A solution of PdCl_4 in acetone was prepared by oxidizing PdCl_2 in acetone containing a little HCl by chlorine.¹ 0.43 g (~ 2.9 mmole) sample of the ligand (TU) was dissolved in 85 ml of ethanol. This was slowly added to 50 ml intense red coloured solution of PdCl_4 containing 1 mmole of the salt, whereupon a bright orange coloured precipitate appeared. It was centrifuged, washed successively with hot acetone, ethanol and ether. It was dried in an air oven at 120 °C for eight hours, yielding a bright orange coloured complex.

Anal. Calcd. for $\text{Pd}_2(\text{TU})_5\text{Cl}_2$: C, 23.9; H, 1.6; N, 13.9; S, 31.8; Pd, 21.1; Cl, 6.9. Found: C, 23.7; H, 1.9; N, 13.7; S, 31.5; Pd, 20.9; Cl, 6.6.

(e) Bis(2,4-dithiouracil)platinum(II).— A solution of the ligand 0.3 g (~ 2 mmole) in 50 ml of ethanol was mixed with 50 ml solution of K_2PtCl_4 (0.42 g) in distilled water. The mixture was stirred whereupon a yellow precipitate appeared. It was digested for about one hour on a water bath. The precipitated complex was centrifuged, washed successively with hot water, ethanol and finally, with

ether. It was dried in an air oven at 120°C for fourteen hours, yielding a yellow complex.

Anal. Calcd. for $\text{Pt}(\text{TU})_2$: C, 20.0; H, 1.2; N, 11.7; S, 26.7; Pt, 40.7. Found: C, 19.8; H, 1.5; N, 11.5; S, 26.3; Pt, 40.4.

(f) Bis(2,4-dithiouracil)dichloroplatinum(IV).— 0.3 g sample of the ligand (~ 2 mmole) was dissolved in 50 ml of ethanol and 0.4 g of K_2PtCl_6 (~ 1 mmole) in 50 ml of very dilute hydrochloric acid. The two solutions were mixed. On stirring, a yellow precipitate appeared. It was digested for about an hour on a water bath.

The precipitated complex was centrifuged, washed successively with hot water ethanol and finally, with ether. It was dried for a few hours in an air oven at 120°C , yielding a yellow complex.

Anal. Calcd. for $\text{Pt}(\text{TU})_2\text{Cl}_2$: C, 17.3; H, 1.4; N, 10.1; S, 23.1; Pt, 35.1; Cl, 12.8. Found: C, 17.6; H, 1.6; N, 10.4; S, 23.5; Pt, 35.5; Cl, 12.4.

Analyses

The analyses of the metal ions and the halogen were carried out by the standard methods,^{2,3} Carbon, hydrogen, and nitrogen analyses were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur, India. The analytical results are given in the text.

Infrared, magnetic susceptibility and visible spectra of the ligand and the complexes were taken by the usual procedure described

in Chapter II. The major bands of the infrared spectra and their assignments are given in Table I. Solubilities, the magnetic moments and the positions of the electronic spectral bands are given in Table II.

RESULTS AND DISCUSSION

From the analytical data (given in the text) and comparison of the stoichiometries with the known preference of Pd(II), Pt(II), Pt(IV), Pd(IV), Rh(III) and Ru(III) for a coordination of four or six, it is apparent that the ligand is functioning as a bidentate in all the complexes. In such a situation it can form either a simple salt by substituting the protons bonded to the nitrogen atom, or an inner complex or a polymer by linking through thiocarbonyl sulphur and nitrogen atoms (structures are given in Chapter II). The ligand is assumed to be present in thione form (reason cited in Chapter II of the thesis).

The positions of the main infrared absorption bands of the ligand along with their major shifts after complexation are given in Table I. Since the thioamide groups were believed to take part in the bond formation with the metal ions in complexes, one should expect the major shifts in the positions of the bands arising due to the stretching of the bonds and the bending of the angles of the two H-N-C-S groups of the ligand. Also due to the presence of the two HNCS groups adjacent to each other, the thioamide bands will be either

split ones, or broad due to the intramolecular interaction. The major shifts along with the discussion are summarized below:

(a) In the spectra of the complexes, the major changes in the positions of the bands arising due to the stretching of the bonds and bending of the angles of two H-N-C-S groups are similar to those of cobalt(II) and thallium(I), complexes (Chapter II). This indicates that in these complexes, (i) the ligand is acting as bidentate, and (ii) the bonding with the metal ions in the complexes are through thiocarbonyl sulphur and nitrogen of the deprotonated N-H group.

(b) In the regions $320-350\text{ cm}^{-1}$ and $450-490\text{ cm}^{-1}$, there appear two new moderately intense bands in the spectra of all the complexes. These bands can not be assigned to either pure ν (M-S) or ν (M-N) modes of vibrations respectively. Both these bands must be having contributions from ν (M-S), ν (M-N) and other skeletal modes of vibration characteristic of pyrimidine ring. However, it is very probable that the bands in the region $320-350\text{ cm}^{-1}$ and $450-490\text{ cm}^{-1}$ are having maximum contribution from ν (M-S) and ν (M-N) respectively.

(c) In the case of Rh(III) and Ru(III) complexes, a new band appears in the region $\sim 270\text{ cm}^{-1}$. This is assigned⁴ to ν (M-Cl) of the bridging group M-Cl-M.

From the preceding discussion of the infrared spectra of the complexes and the ligand, it can be inferred: (i) that the ligand

is acting as a bidentate in these complexes, (ii) that there is metal-chlorine bridge in the Rh(III) and Ru(III) complexes, and (iii) that the ligand is in the thione form. It is very hard to distinguish if the complexes are having the inner type of structure or polymeric structure. However, the complexes are highly insoluble in all the common organic and inorganic solvents. From this observation the possibility of the polymeric structure is more than that of the inner type. Therefore polymeric structures are proposed for these complexes.

Visible Spectra and Magnetic Properties

The electronic spectra of the complexes in the visible region were studied to determine the possible spatial arrangements of the donor atoms around the metal ions. All the complexes start absorbing continuously from 8000 cm^{-1} . However, there are a number of shoulders present in the spectra at various wave numbers (Table II).

Owing to the greater oxidizing power of the metal ions of the IVth and Vth transition series, and also owing to the greater reducing power of the sulphur containing ligands, the charge transfer bands appear at much lower wave number,⁵ due to the transitions between the various molecular orbitals of the complex ion. Besides the extinction coefficients of these bands in the spectra of the IVth and the Vth transition series, metal ions are large. Therefore, it will not be possible to make definite assignments to the bands which appear as shoulder, although some of them appear in the expected region.

Thus, in Pt(II) and Pd(II) complexes, a broad band is present around 24,400 cm^{-1} and 22,000 cm^{-1} respectively. These ^{bands} in the square planar geometry of the donor atoms around metal ions can be assigned to the transition $^1A_{1g} \longrightarrow ^1B_{1g}$ ($a_{1g}^2 \longrightarrow a_{1g}^1 b_{1g}^1$). In the spectra of Rh(III) complex, a shoulder appears at 13,200 cm^{-1} , which may be assigned to $^1A_{1g} \longrightarrow ^1T_{1g}$ with an energy interval equal to $-35F_4 + 10Dq$, when rhodium(III) is surrounded by an octahedral field.

The spectra of all the complexes show two bands in the region 33,000 cm^{-1} and 25,000 cm^{-1} which have been assigned to $n \longrightarrow \pi^*$ transitions of the thiocarbonyl groups of the ligand molecule. These bands appear in the spectra of the ligand at 33,000 and 26,300 cm^{-1} .

The complexes of Rh(III), Pd(II), Pt(II), Pt(IV) and Pd(IV) are diamagnetic indicating octahedral geometry around Rh(III), Pd(IV) and Pt(IV) and square planar geometry for Pt(II) and Pd(II) metal ions. These spatial arrangements around the metal ions are well in correspondence with the known preferred arrangements of the ligand molecules around metal ions.¹

The magnetic moment of ruthenium(III) complex is 0.99 B.M., which is much lower than that due to one unpaired electron. This indicates that there is a little spin-spin interaction between two ruthenium ions which impart antiferromagnetic character to the complex. On this basis we propose a long metal-metal bond in the complex.

Thus, on the basis of analytical, infrared, visible spectral and magnetic data the structures I, II, III, IV, & V have been proposed for the complexes.

Table I

Assignments of the Major Infrared Bands of the Ligand and the Complexes (cm^{-1})

Ligand	Complexes ^a	Assignments
3220(s) 3165(s) 3070(b) 2880(b)	2920(b) 3060 3140(b)	Coupled vibration due to ν (CH) and ν (N-H)
1605(s, sh)	1600(m, sh)	δ (N-H) + ν (C=C), containing major contribution from ν (C=C)
1565(s, b) 1480(m, s, sh)	1540 1500	Thioamide band I ^b
1210(s) 1230(s) 1250(s)	1190 1200 1220	Thioamide band II ^c
1128(s, sh) 1085(s, sh)	1150 1100	Thioamide band III ^d
780 795	820(b)	Thioamide band IV ^e
-	450-490	Vibration having major contribution from ν (M-N) ^f
-	320-350(one)	Vibration having major contribution from ν (M-S) ^f
-	\sim 270	ν (M-Cl-M) bridge ^g

a) These wave numbers represent only the region where the metal ion complexes absorb; b) due to δ (N-H) + ν (C-N) + ν (C=C); c) due to δ (N-H) + ν (C-N) + δ (C-H); d) mainly due to ν (C-N) + ν (C=S); e) mainly due to ν (C=S); f) the position of these bands vary with the metal ions; g) this band is present only in Rh(III) and Ru(III) complexes.

Table II

Solubilities, the Position of the Electronic Spectral band
in the Ligand and the Complexes and their Magnetic Moments

Complexes and ligand	μ_{eff} B.M.	Solubi- lity	Position of the absorp- tion band in cm^{-1}
$\text{C}_4\text{H}_4\text{N}_2\text{S}_2(\text{TU})$	-	-	33,000 26,300
(a) $\text{Rh}(\text{TU})_2\text{Cl}$	D	I	32,258 26,316 13,200 12,345 10,000
(b) $\text{Ru}_2(\text{TU})_5\text{Cl}$	0.99	I	28,985 27,777 14,285 13,689 13,151 9,803
(c) $\text{Pd}(\text{TU})_2$	D	I	25,000 22,000 11,111
(d) $\text{Pd}_2(\text{TU})_5\text{Cl}$	D	I	33,000 - 20,000 (broad band)
(e) $\text{Pt}(\text{TU})_2$	D	I	29,412 24,400 16,667 - 12,500 (broad band)
(f) $\text{Pt}(\text{TU})_2\text{Cl}_2$	D	I	30,037) (broad 29,412) band)

D) Diamagnetic; I) Insoluble in chloroform, carbontetrachloride, benzene, tetrahydrofurane, cyclohexane, xylene, toluene, acetone, methanol, dioxane, dichloroethane and dichloromethane.

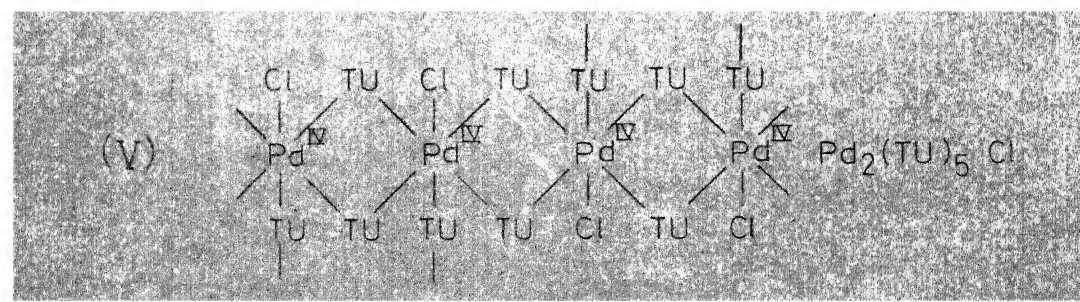
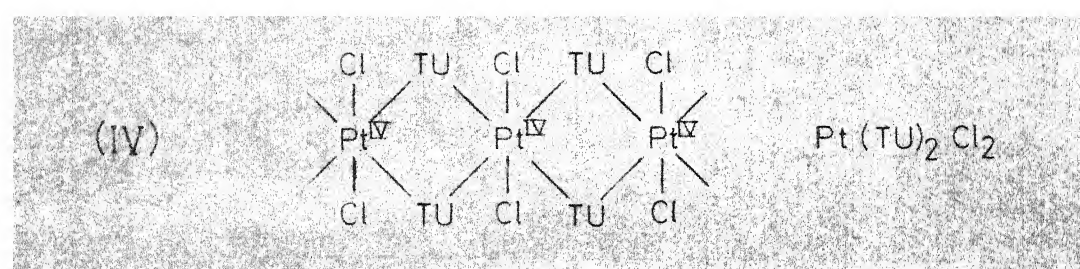
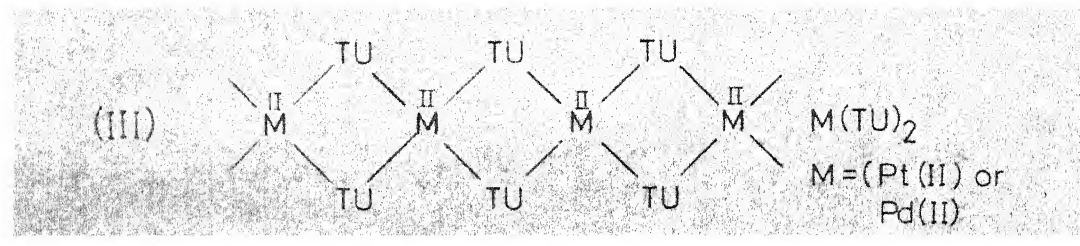
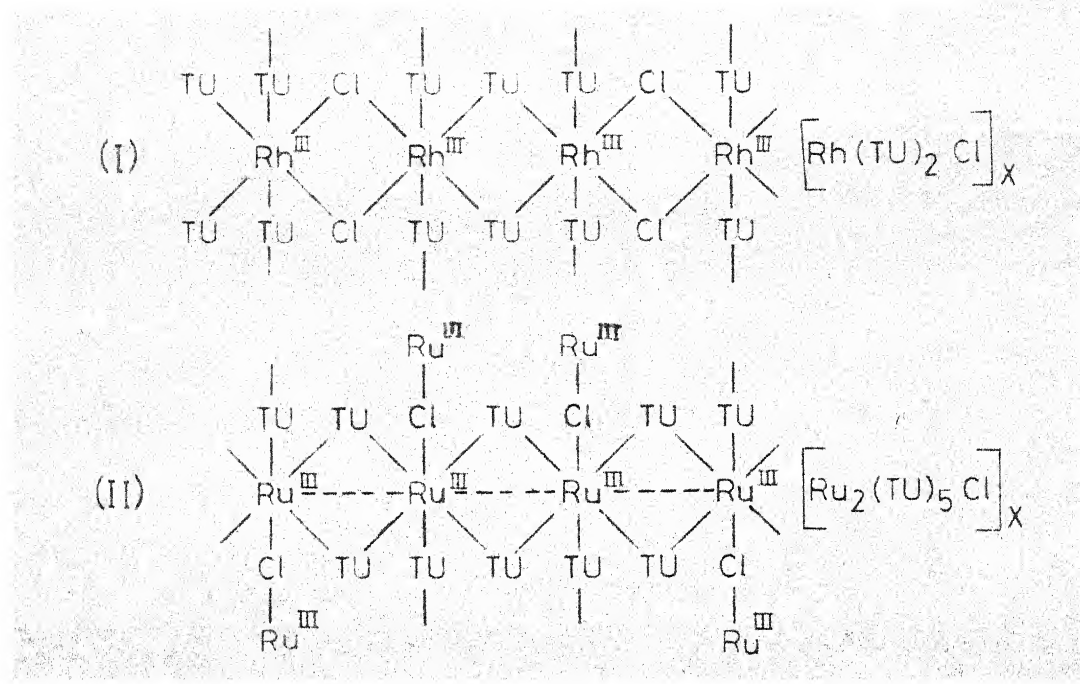


Fig. III.1

1. 2,4-Dithiouracil
2. $\text{Rh}(\text{TU})_2\text{Cl}$
3. $\text{Ru}_2(\text{TU})_5\text{Cl}$
4. $\text{Pd}(\text{TU})_2$
5. $\text{Pd}_2(\text{TU})_5\text{Cl}_2$
6. $\text{Pt}(\text{TU})_2$
7. $\text{Pt}(\text{TU})_2\text{Cl}_2$

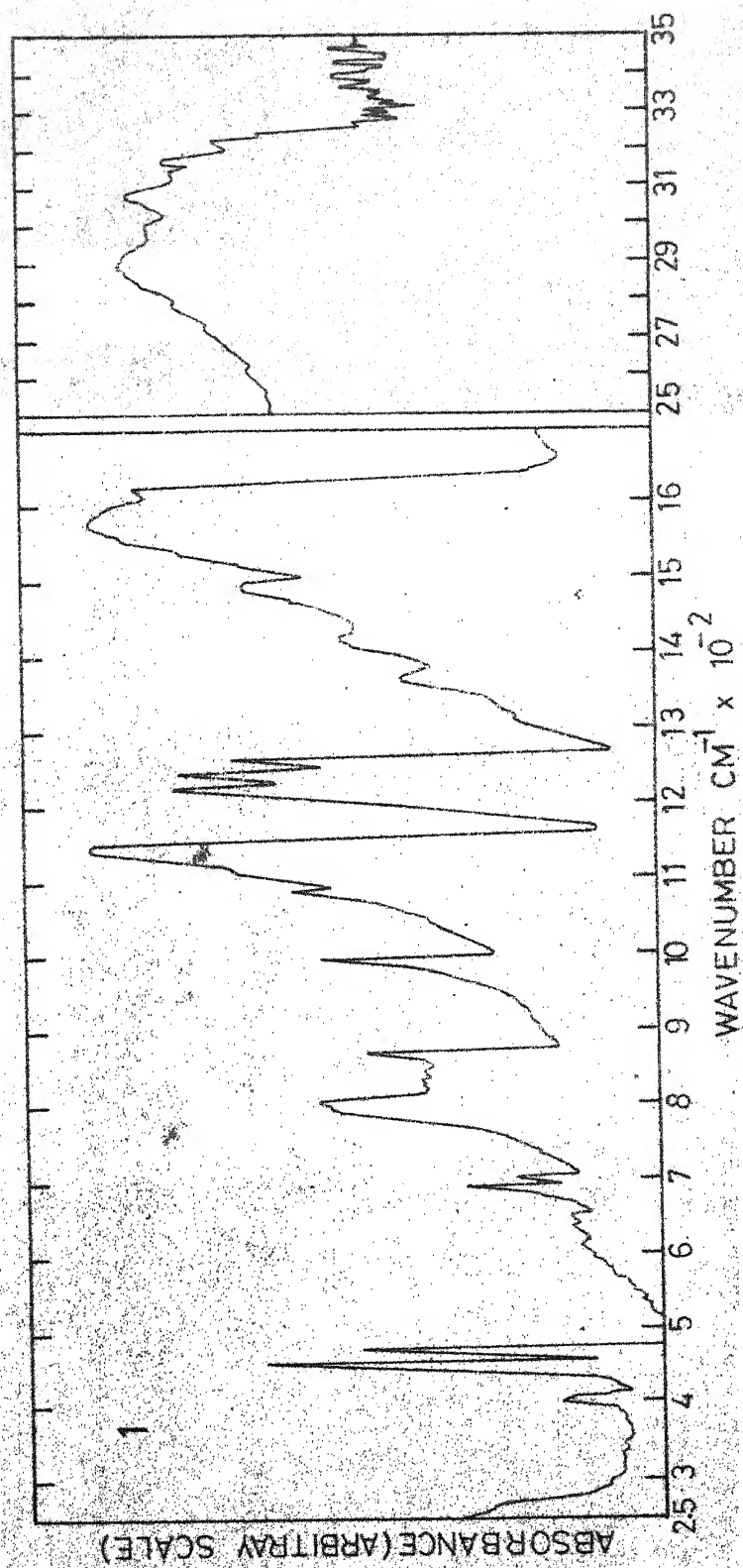


Fig. III.1

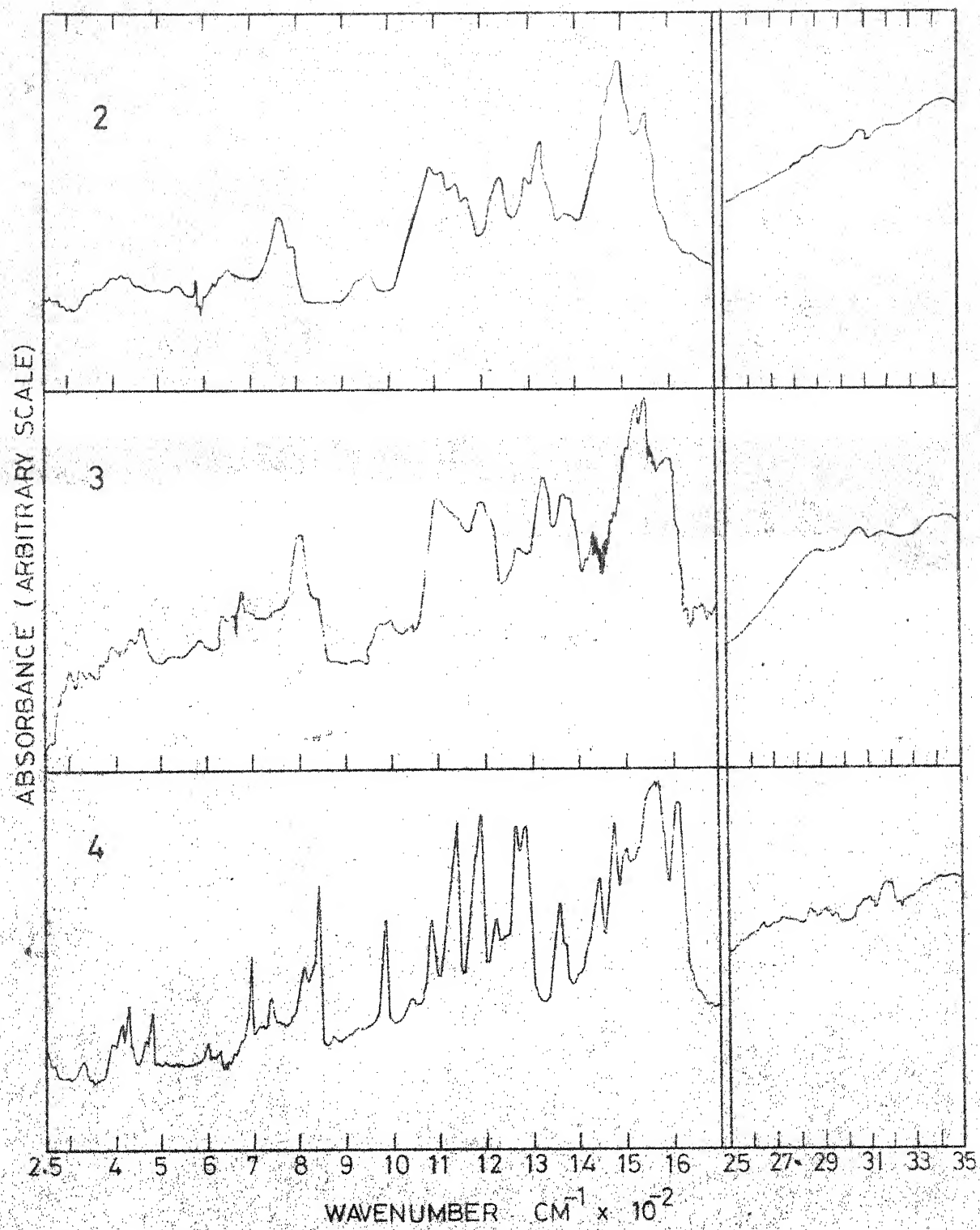


Fig. III.1

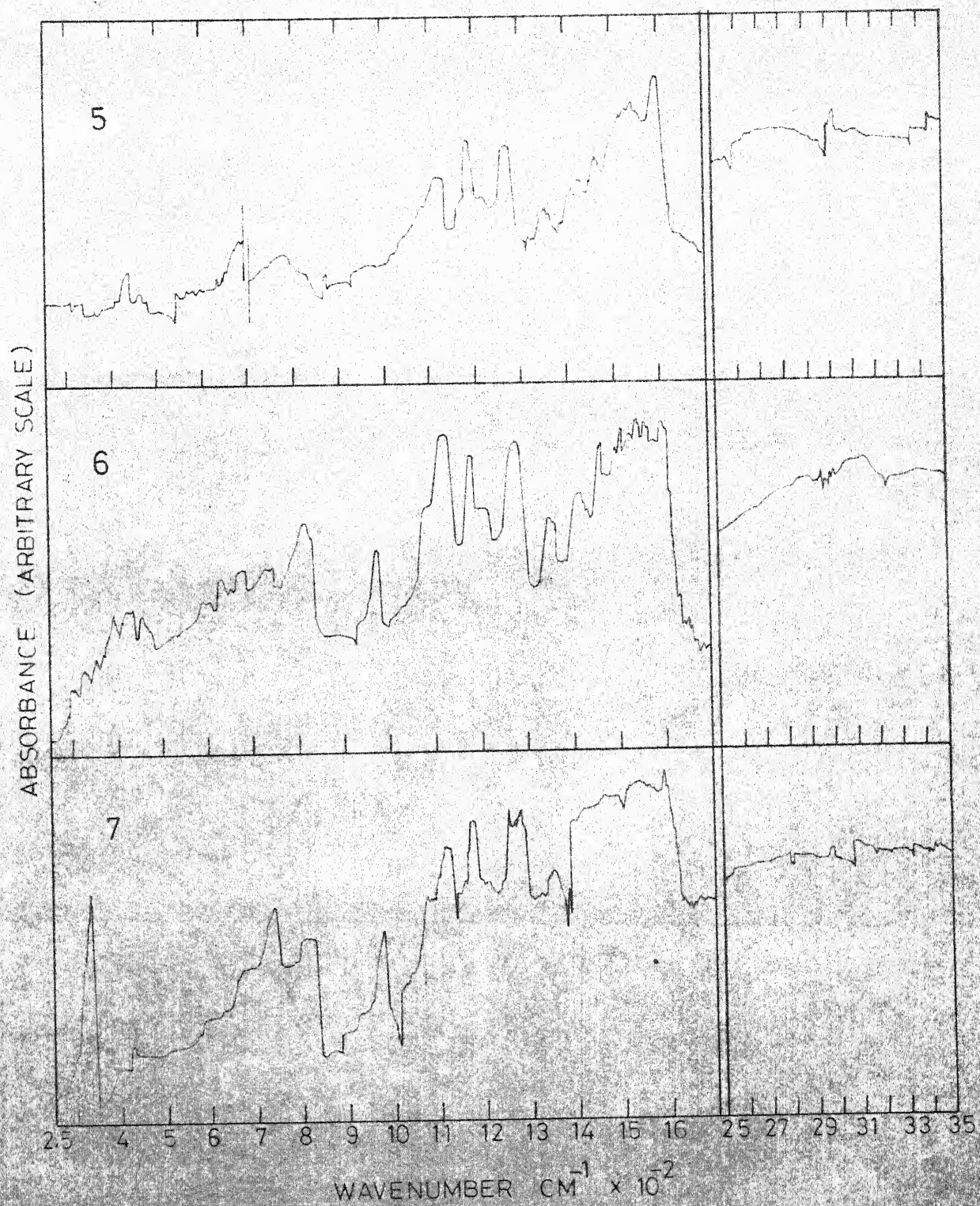


Fig. III.1

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EXPERIMENTAL

Preparation of Metal Complexes

(a) Bis(2,4-dithiouracil)bis-(triphenylphosphine)palladium(0).- Tetrakis-(triphenylphosphine)palladium(0) was prepared by the published procedure.¹ 0.40 g sample of $\text{Pd}(\text{P}\phi_3)_4$ (~ 0.34 mmole) was dissolved in 70 ml of benzene at about 70°C . To this, another solution of 0.8 g of the ligand (~ 5.5 mmole) in 100 ml of boiling *n*-butanol was added dropwise. The resulting solution was concentrated on a water bath to a small volume which resulted in a reddish orange coloured precipitate. The resulting complex was centrifuged and washed successively with *n*-butanol, benzene, ethanol and finally, with ether. It was dried in a vacuum dessicator for about ten hours, yielding a reddish orange coloured complex.

Anal. Calcd. for $\text{Pd}(\text{TUH})_2(\text{P}\phi_3)_2$: C, 57.7; H, 3.7; N, 6.1; S, 14.0; Pd, 11.5. Found: C, 57.3; H, 3.2; N, 5.9; S, 13.6; Pd, 11.1.

(b) Tetrakis(2,4-dithiouracil)bis(triphenylphosphine)dichlorotrirrhodium(I).- Tris(triphenylphosphine)monochlororhodium(I) was prepared by the known procedure.² A solution of 0.46 g of the $\text{Rh}(\text{P}\phi_3)_3\text{Cl}$ (~ 0.6 mmole) was prepared in 70 ml of benzene. To this, a solution of 0.69 g of the ligand (~ 4.7 mmole) in 80 ml of *n*-butanol was added dropwise. The mixture was heated on a water bath at about 80°C for four hours and the precipitated complex was filtered out and washed successively with hot *n*-butanol, benzene, ethanol and finally, with ether. It was dried in an air oven at 120°C for a few hours, yielding an orange yellow coloured complex.

Anal. Calcd. for $\text{Rh}_5(\text{TUH})_3(\text{TU})\text{Cl}_2(\text{P}\phi_3)_2$: C, 42.1; H, 2.7; N, 7.5; S, 17.2; Rh, 28.8; Cl, 4.7. Found: C, 41.2; H, 2.2; N, 8.0; S, 16.7; Rh, 29.3; Cl, 4.4.

(c) Tetrakis(2,4-dithiouracil)diaquodirrhodium(II).— $\left[\text{Rh}(\text{II})(\text{CCl}_3\text{COO})_2\right]_2$ complex was prepared by a slightly modified Winkhaus and Ziegler method.³ The greenish blue crystals, thus obtained, were dissolved in about 50 ml of n-butanol. The resulting solution was mixed with a solution of 0.3 g of the ligand (~ 2 mmole) in 50 ml of n-butanol and heated on a water bath at 60–70°C for about three hours. The precipitated complex was filtered out and washed successively with boiling n-butanol, ethanol, and finally, with ether. It was dried in an air oven at 120°C for a few hours, yielding a brown complex.

Anal. Calcd. for $[\text{Rh}(\text{TU})_2\text{H}_2\text{O}]_2$: C, 23.4; H, 1.9; N, 13.6; S, 31.2; Rh, 25.1. Found: C, 22.9; H, 1.8; N, 13.4; S, 31.5; Rh, 24.9.

(d) Tris(2,4-dithiouracil)diaquodiruthenium(II).— The $\text{Ru}(\text{II})$ complex $(\text{Ru}_5\text{Cl}_{12})^{-2}$ was first obtained as a deep blue species by Wilkinson, et al. method.⁴ To this, 0.80 g ^{of} the ligand (~ 5.5 mmole) in 100 ml of ethanol was added. The mixture was refluxed for two hours. The precipitated complex was filtered out and washed successively with water, ethanol and finally, with ether. It was dried in an air oven at 120°C, yielding a dark brown coloured complex.

Anal. Calcd. for $\text{Ru}_2(\text{TUH})_3(\text{H}_2\text{O})_2$: C, 21.3; H, 1.9; N, 12.5; S, 28.5; Ru, 30.1. Found: C, 21.5; H, 2.0; N, 12.8; S, 28.1; Ru, 29.7.

Oxidation State of Metal Ions

Oxidative reaction of palladium(0) complex with iodine.— The reaction of $\text{Pd}(\text{TUH})_2(\text{P}\phi_3)_2$ with alcoholic iodine was carried out according to the method given by Malatesta.⁵ An exact weight of the complex and an excess of standard alcoholic solution of iodine (N/50) were shaken for one hour and then allowed to keep for a few hours in a well stoppered flask. The unreacted iodine was titrated with a standard solution of sodium thiosulphate (N/50). Another blank titration was carried out without the addition of the complex but in the presence of an equivalent amount of triphenylphosphine and the ligand (TUH). The difference of the two titer readings indicated the two electron change per mole of complex in the reaction.

Oxidation reaction of rhodium(I) and rhodium(II) complexes with ceric ammonium sulphate.— The oxidation states of the metal ions were determined by the procedure described in the literature.⁶ A known weight of the complex was allowed to react with a measured volume of ceric ammonium sulphate solution standardized with pure iron metal in presence of platinum, which acts as a catalyst. Dissolved air in the ceric ammonium sulphate solution was removed by presaturating it with nitrogen. The rest of the method is the same as described in palladium(0) case. The unreacted ceric ammonium sulphate solution was determined with

standard ferrous ammonium sulphate solution using ferroin as indicator. Rh(I) complex titrated for two electron change and Rh(II) complex for one electron change.

Methods and Techniques

The analyses of the metal ions, chloride and sulphur were carried out by the standard methods.^{7,8} Carbon, hydrogen, and nitrogen analyses were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur-16, India. The analytical results are given in the text.

The infrared spectra, magnetic susceptibility measurements and visible spectra of the ligand (TUH) and the complexes have been taken by the procedure described in Chapter II. The major bands of the infrared spectra are given in Table I. The results of magnetic moments of the complexes, the position of the visible absorption band and their solubilities in the solvents are given in Table II.

RESULTS AND DISCUSSION

Palladium(0) Complex

The analytical results show that the formula of the palladium(0) complex is $\text{Pd}(\text{TUH})_2(\text{P}\phi_3)_2$. The oxidation reduction reaction with iodine indicates that two equivalents of iodine are needed to oxidize one equivalent of the complex suggesting palladium to be in the zero-oxidation state. Palladium in the zerovalent state prefers to have tetrahedral arrangement of

the ligands. Assuming this, it is apparent that the ligand in this complex is functioning as a monodentate. In such a situation it can form bond with palladium by linking through nitrogen or sulphur of the thiocarbonyl group (the ligand is assumed to be in the thione form). In the infrared spectrum of the complex there is no appreciable change in the position of the 3220 cm^{-1} , 3165 cm^{-1} , 3070 cm^{-1} and 2880 cm^{-1} bands ($\sim 10\text{ cm}^{-1}$). However, due to the presence of $\nu(\text{C-H})$ of the triphenylphosphine around 3000 cm^{-1} , 2880 cm^{-1} and 3070 cm^{-1} bands broaden. Similarly the position of the thioamide bands I and II (1565 cm^{-1} , 1480 cm^{-1} and 1210 cm^{-1} , 1230 cm^{-1} and 1250 cm^{-1}) are not much shifted in the spectra of the complex ($\sim 10\text{ cm}^{-1}$). However, the bands due to thioamide band (III) (1128 cm^{-1} , 1085 cm^{-1}) which contains contribution from $\nu(\text{C-N})$ and $\nu(\text{C=S})$ are split into two bands and also the positions of these bands are shifted by about 20 cm^{-1} . Similarly, the positions of the bands at 780 cm^{-1} and 795 cm^{-1} (thioamide band IV) are shifted to 775 cm^{-1} and 835 cm^{-1} and both these bands are split into two bands. The shifts and the split in the thioamides bands III and IV indicate that probably the bonding of palladium is through thiocarbonyl sulphur and not through nitrogen of the ligand.

All the bands of the triphenylphosphine are present in the i.r. spectrum of the complex. However, there appear two new sharp and strong bands at 745 cm^{-1} and 735 cm^{-1} in the spectrum. Such bands are characteristic of phosphorus compounds in which it achieves coordination number four. Thus, the presence of these bands indicate

the coordination of phosphorus to palladium. A new band around 300 cm^{-1} in the spectrum may be assigned to ν (Pd-S).

The palladium complex is diamagnetic indicating the singlet ground state. In case the palladium in the complex is in zerovalent state as indicated by the oxidation reduction reaction and also supported by i.r. spectrum, one should not expect any band in the visible spectrum due to d-d transition (d^{10} system). The spectrum of the Pd(0) complex shows only one strong band below $400\text{ m}\mu$ which may be due to the ligand molecules. Thus, the complete absence of the absorption bands in the visible region, independently suggests that the metal in the complex is present in the zerovalent state. Based on these data, the tetrahedral structure I is proposed for the complex.

Rhodium(I) Complex

The analytical data of rhodium(I) suggest the formula of the complex to be $\text{Rh}_3(\text{TUH})_3(\text{TU})\text{Cl}_2(\text{P}\phi_3)_2$. It appears that one of the four ligand molecules is linked with rhodium after deprotonation. Most of the rhodium(I) complexes are square planar,⁹ and therefore we expect that the geometry around rhodium(I) in this complex is also square-planar.

The i.r. spectrum of the complex is similar to that of palladium(0) complex except that thioamide bands (I) and (II) are broadened. Since thioamide bands I and II contain mostly δ (N-H), and if one of the ligand molecules is deprotonated during complex

formation, one should expect shift in the thioamide bands (I) and (II) of the deprotonated ligand, while other ligand molecules should show thioamide bands (I) and (II) at about the same position as that of palladium(0) complex. This shift in the position of the thioamide bands (I) and (II) at 780 cm^{-1} is split into two bands (795 cm^{-1} and 820 cm^{-1}) and that at 795 cm^{-1} is broadened, indicating the two types of C=S group.

The complex is diamagnetic indicating the singlet ground state, which would be expected by analogy with other complexes of univalent rhodium.¹⁰ This suggests the square-planar surrounding around rhodium. Assuming square planar arrangement, three spin allowed d-d transitions are anticipated in the spectrum of the complex. Besides these, the spectrum should show three spin forbidden singlet-triplet transitions from $^1A_{1g}$ to $^3A_{2g}$, $^3B_{1g}$ and 3E_g respectively. However, the spectrum in the nujol mull shows one moderately strong band at $580\text{ m}\mu$ ($17,000\text{ cm}^{-1}$) and two weak bands at $760\text{ m}\mu$ ($\sim 13,170\text{ cm}^{-1}$) and $800\text{ m}\mu$ ($\sim 12,500\text{ cm}^{-1}$). Generally one ascribes the most intense and highest energy d-d band to the $^1A_{2g} \rightarrow ^1E_g$ transition¹¹ and the low energy weak transition, to spin forbidden transition, which have gained intensity through spin orbit coupling. Based on this, $17,000\text{ cm}^{-1}$ band is assigned to $^1A_{1g} \rightarrow ^1E_g$ and the bands at $13,170\text{ cm}^{-1}$ and $12,500\text{ cm}^{-1}$ to two out of three spin forbidden transitions. However, it will be very difficult to assign these two spin forbidden bands. The position of the band at

$17,000\text{ cm}^{-1}$ also corresponds to the one observed in other Rh(I) complexes.¹² Based on these data structure II has been tentatively proposed for the complex.

Rhodium(II) Complex

The analytical data indicate its formula to be $[\text{Rh}(\text{TU})_2(\text{H}_2\text{O})]_2$. The oxidation state of rhodium was found to be +2 by ceric ammonium-sulphate oxidation reaction.

The i.r. spectrum of the complex shows shifts in the position of the bands similar to the ones found in the spectrum of Pt(II), Pd(II) and other metal ion complexes in which ligand is acting as a bidentate (Chapter III) suggesting the bidentate nature of the ligand in this complex. Besides this, there are bands at $3400\text{ cm}^{-1}(\text{b})$, $1650\text{ cm}^{-1}(\text{w})$ and $880\text{ cm}^{-1}(\text{mst})$ which may be assigned to the characteristic bands of the coordinated water.¹³

The complex is diamagnetic. The quenching of the magnetic moments in the d^7 system could be explained either by assuming strong spin-spin interaction, which might arise due to rhodium(II)-rhodium(II) linkage with the formation of either a δ -bond by the overlap of $d_{x^2-y^2}$ orbitals^{14,15} or a σ bond by the overlap of d_z^2 orbital¹⁶ or by superexchange mechanism. It has been shown, however, that similar known diamagnetic Rh(II) complexes,^{17,18} have a short rhodium-rhodium distance forming a direct metal-metal bond. The superexchange phenomenon generally takes place in those compounds in which two metal

atoms are linked through a monoatomic bridge. Assuming this, a direct metal-metal bond is postulated to explain the quenching of paramagnetism. Diamagnetic complexes have also been reported earlier,^{6,19,20} in which spin-spin interaction between two adjacent metal ions have been postulated.

The visible spectrum of the complex shows one band at $17,700\text{ cm}^{-1}$ which could not be definitely assigned in the absence of the energy level diagram of such diamagnetic rhodium(II) complexes. However, analogous to the other diamagnetic rhodium(II) complexes, which show a band around $18,000\text{ cm}^{-1}$, a band appears at $17,700\text{ cm}^{-1}$ in this complex also.

Thus, on the basis of the above discussion of the i.r. and magnetic data structure (III) has been proposed for the rhodium(II) complex, which is analogous to its carbonylate complex.¹⁸

Ruthenium(II) Complex

The formula of the complex is $\text{Ru}_2(\text{TUH})_3(\text{H}_2\text{O})_2$ as suggested by the analytical data.

The i.r. spectrum of the complex is similar to cadmium complex, where ligand is acting as a tetradentate (Chapter II). Besides, there are weak bands present due to $\nu(\text{N-H})$ around 3100 cm^{-1} . But these bands are very weak as compared to those present in the spectrum of the ligand that one should expect if one out of the three ligands is not deprotonated in the complex formation. Besides these, the

characteristic bands due to coordinated water are present around $3400\text{ cm}^{-1}(\text{b})$, $1650\text{ cm}^{-1}(\text{w})$ and $880\text{ cm}^{-1}(\text{mst})$ indicating the presence of coordinated water molecule in the complex.

The ruthenium(II) complex is diamagnetic. In most of the ruthenium(II) complexes, ruthenium preferentially has an octahedral geometry.⁹ If one assumes an octahedral symmetry around the metal ion and if the field produced by the ligand is strong, one should expect diamagnetic behaviour by the complex. The nujol mull spectrum of the complex in the visible range shows three bands at $20,410\text{ cm}^{-1}(\text{m})$, $17,300\text{ cm}^{-1}(\text{m})$ and $12,300\text{ cm}^{-1}(\text{vw})$. There also appears a very weak shoulder at $12,000\text{ cm}^{-1}$. In d^6 system with O_h symmetry, one should expect four bands (two spin allowed bands corresponding to the transition from $^1A_{1g}$ to $^1T_{1g}$ and $^1T_{2g}$ and two spin forbidden bands from $^1A_{1g}$ to $^3T_{1g}$ and $^3T_{2g}$). If the symmetry is lowered, the T_{1g} and T_{2g} levels are split-up further giving a number of other bands (12 bands in all). The two low intensity bands may be tentatively assigned to spin forbidden transition and the bands at $20,410\text{ cm}^{-1}$ and $17,300\text{ cm}^{-1}$ are assigned to $^1A_{1g} \rightarrow ^1T_{2g}$ and $^1A_{1g} \rightarrow ^1T_{1g}$ transition respectively. These are broad bands. Thus, on the basis of i.r., visible spectral and magnetic data, the polymeric structure IV is proposed for the complex.

All the complexes i.e. Pd(0), Rh(I), Rh(II) and Ru(II) are highly insoluble and therefore, the polymeric structures are preferred over mono- or dimeric structures for these complexes.

Table I
The Infrared Bands of the Ligand and the
Complexes of Pd(0), Rh(I), Rh(II) and Ru(II)
(in cm^{-1})

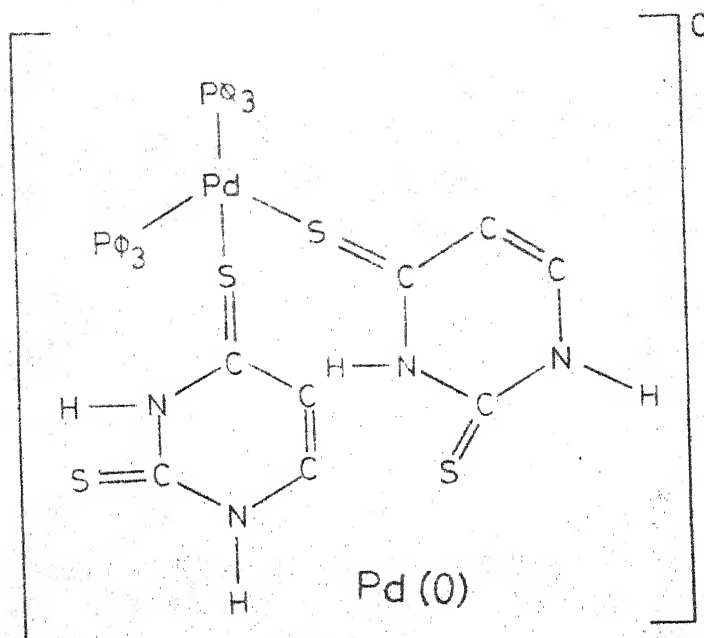
Ligand	Pd(0)	Rh(I)	Rh(II)	Ru(II)
-	-	-	3400(b)	3400(b)
3220(s)	3210	3210	3140(b)	3140(b)
3165(s)	3160	3155	3060	3060
3070(b)	3070	3060	2920(b)	2920(b)
2880(b)	2880	2070	-	-
-	-	-	1650(w)	1650(w)
1605(s, sh)	-	-	1600(m, sh)	1600(m, sh)
1565(s, b)	1555	1555	1540	1540
1480(m, s, sh)	1480	1470	1500	1500
1410	-	-	-	1390
1360	-	-	-	1320
1210(s)	1210	1200	1190	1190
1230(s)	1225	1220	1200	1200
1250(s)	1240	1240	1220	1220
1123(s, sh)	1108	1108	1150	1150
1085(s, sh)	1065	1065	1100	1100
985(m)	-	-	-	885
800(m, sharp)	-	-	880(m, s)	880(m, s)
795	835	795	820(b)	820(b)
780	775	795) 820)	-	600(w)
-	745 735	745 735	-	-
445	-	-	450-490	445
465	-	-	-	435
400	-	-	-	400
-	300	300	330	335

Table II

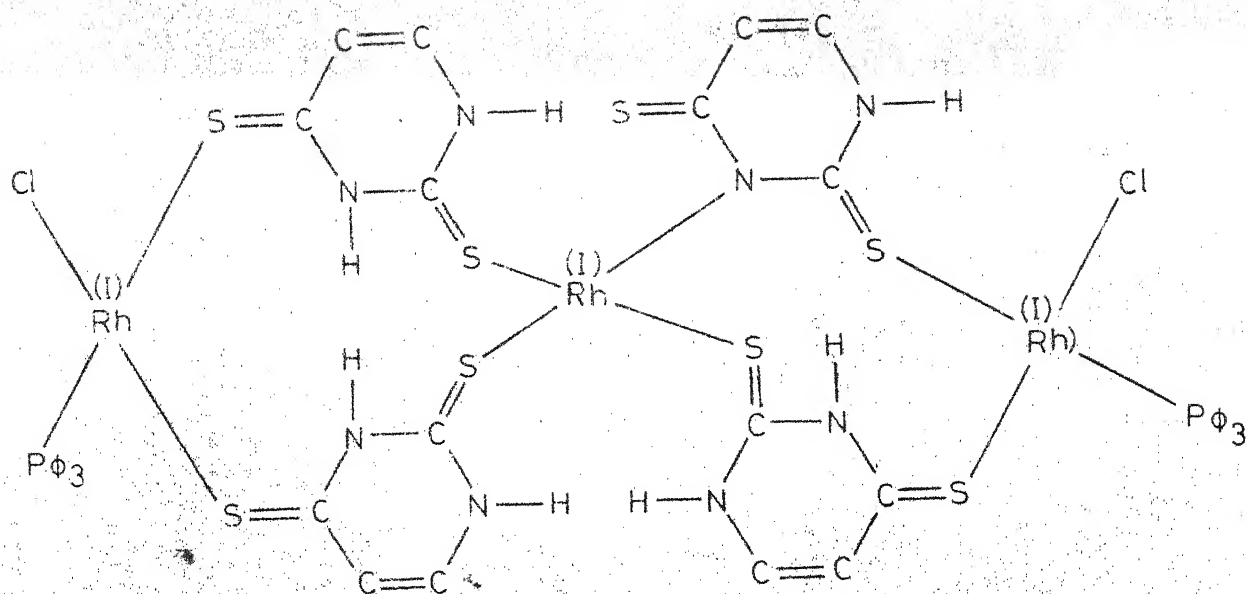
Solubilities, the Magnetic Moments and the
Position of the Visible Absorption Bands
of the Complexes (cm^{-1})

Complexes	Visible absorption band	$\mu_{\text{eff.}}$ B.M.	Solubi- lity
(a) Bis(2,4-dithiouracil)- bis(triphenylphosphine)- palladium(0). $\text{Pd}(\text{TUH})_2(\text{P}\phi_3)_2$	-	D	I
(b) Tetrakis(2,4-dithiouracil)- di(triphenylphosphine)- dichlorotrirrhodium(I). $\text{Rh}_3(\text{TUH})_3(\text{TU})\text{Cl}_2(\text{P}\phi_3)_2$	17,000(s) 13,170(w) 12,500(w)	D	I
(c) Tetrakis(2,4-dithiouracil)- diaquo-dirrhodium(II). $[\text{Rh}(\text{TU})_2\text{H}_2\text{O}]_2$	17,700	D	I
(d) Tris(2,4-dithiouracil)- diaquo-diruthenium(II). $\text{Ru}_2(\text{TUH})_3(\text{H}_2\text{O})_2$	20,410(m) 17,300(m) 12,300(v,w) 12,000(v,w,sh)	D	I

D) Diamagnetic; s) Strong (moderately); w) Weak; v,w) Very weak;
sh) Shoulder; I) Insoluble in chloroform, carbontetrachloride, benzene,
tetrahydrofurane, cyclohexane, xylene, toluene, acetone, methanol,
dioxane, dichloro-ethane, and dichloro-methane.



(I)



Rh(I)

(II)

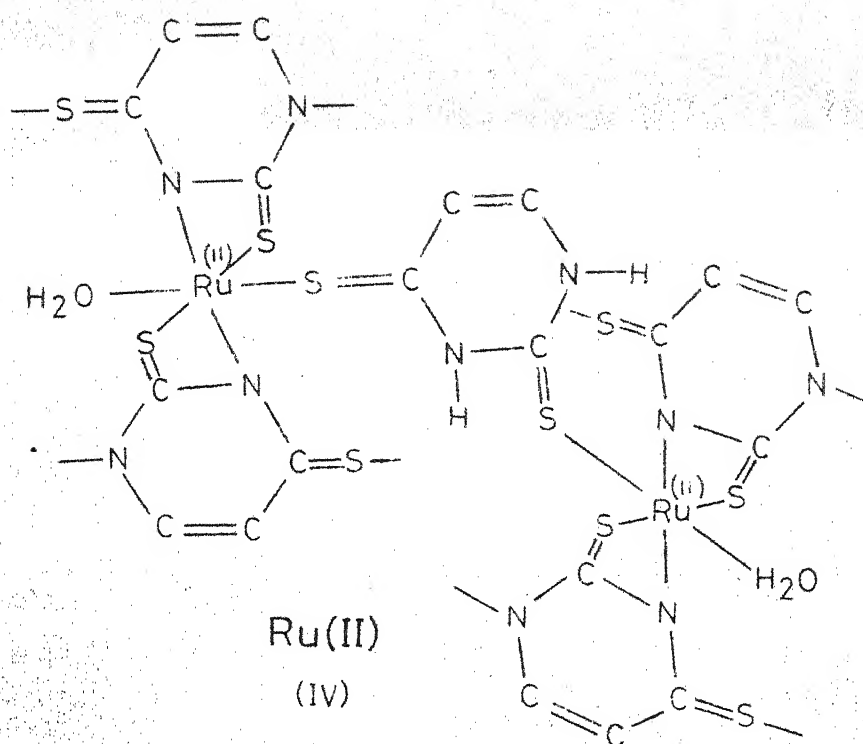
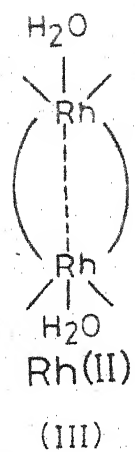


Fig. IV.1

1. 2,4-Dithiouracil
2. $\text{Pd}(\text{TUH})_2(\text{P}\phi_3)_2$
3. $\text{Rh}_3(\text{TUH})_3(\text{TU})\text{Cl}_2(\text{P}\phi_3)_2$
4. $[\text{Rh}(\text{TU})_2\text{H}_2\text{O}]_2$
5. $\text{Ru}_2(\text{TUH})_3(\text{H}_2\text{O})_2$

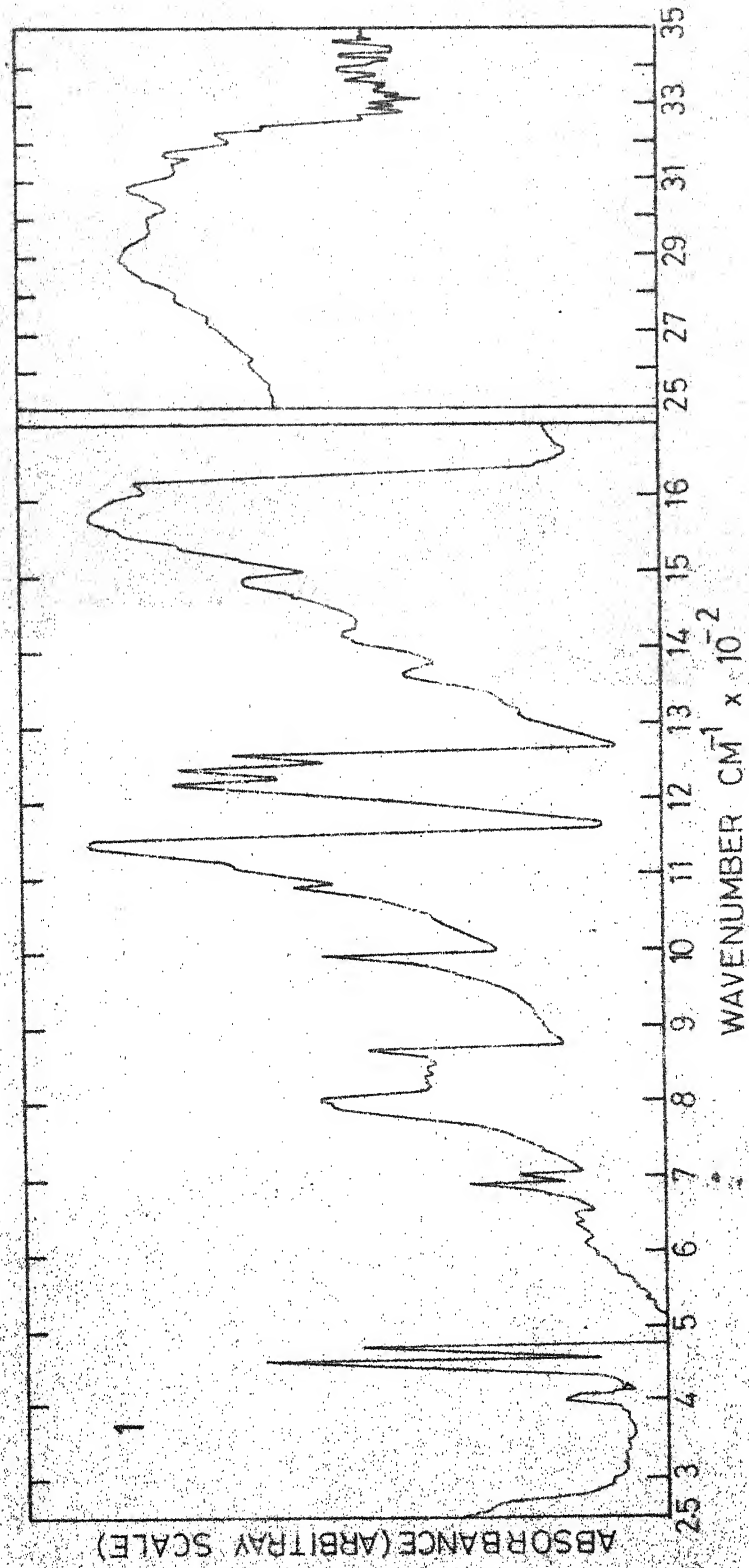
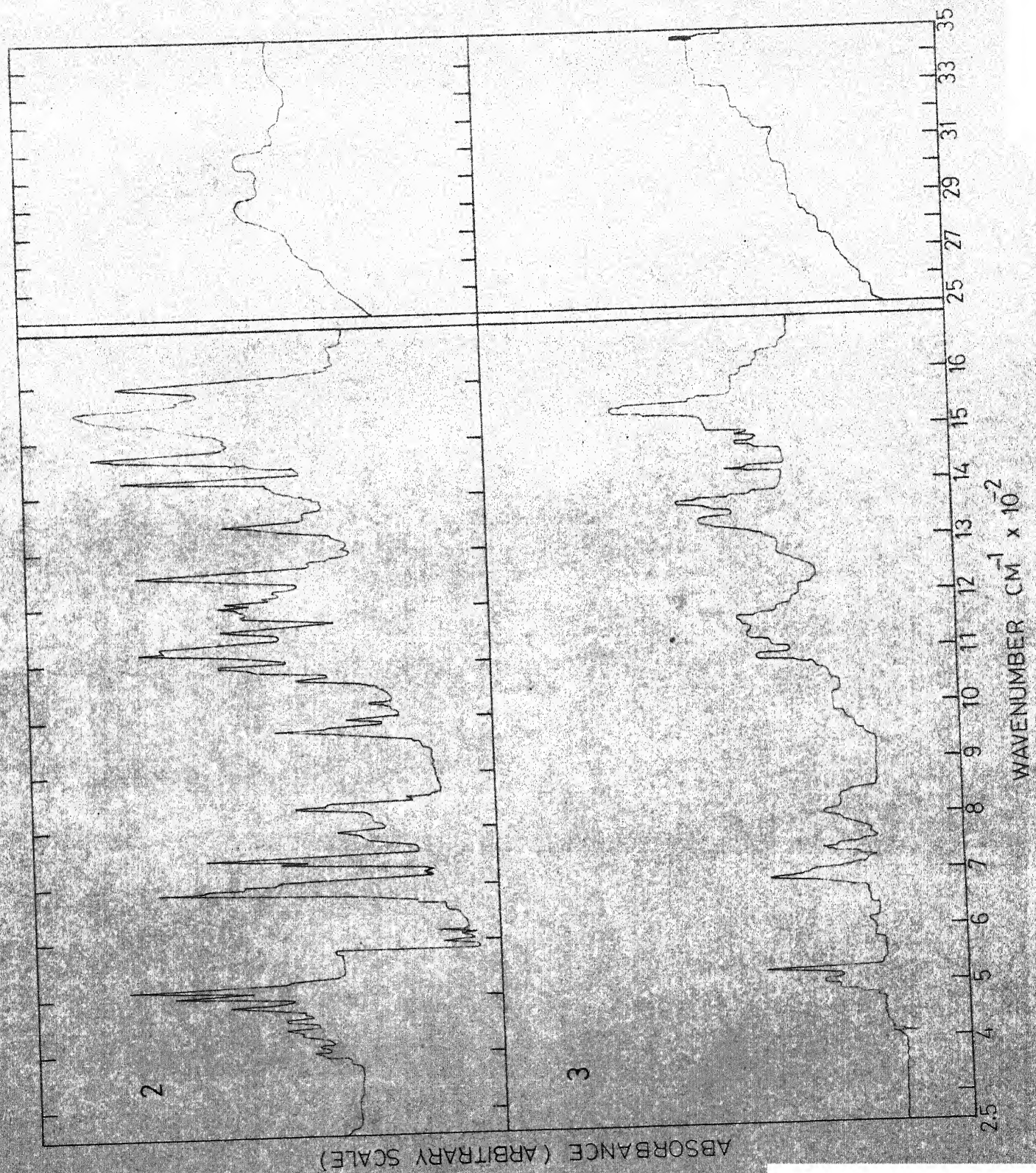
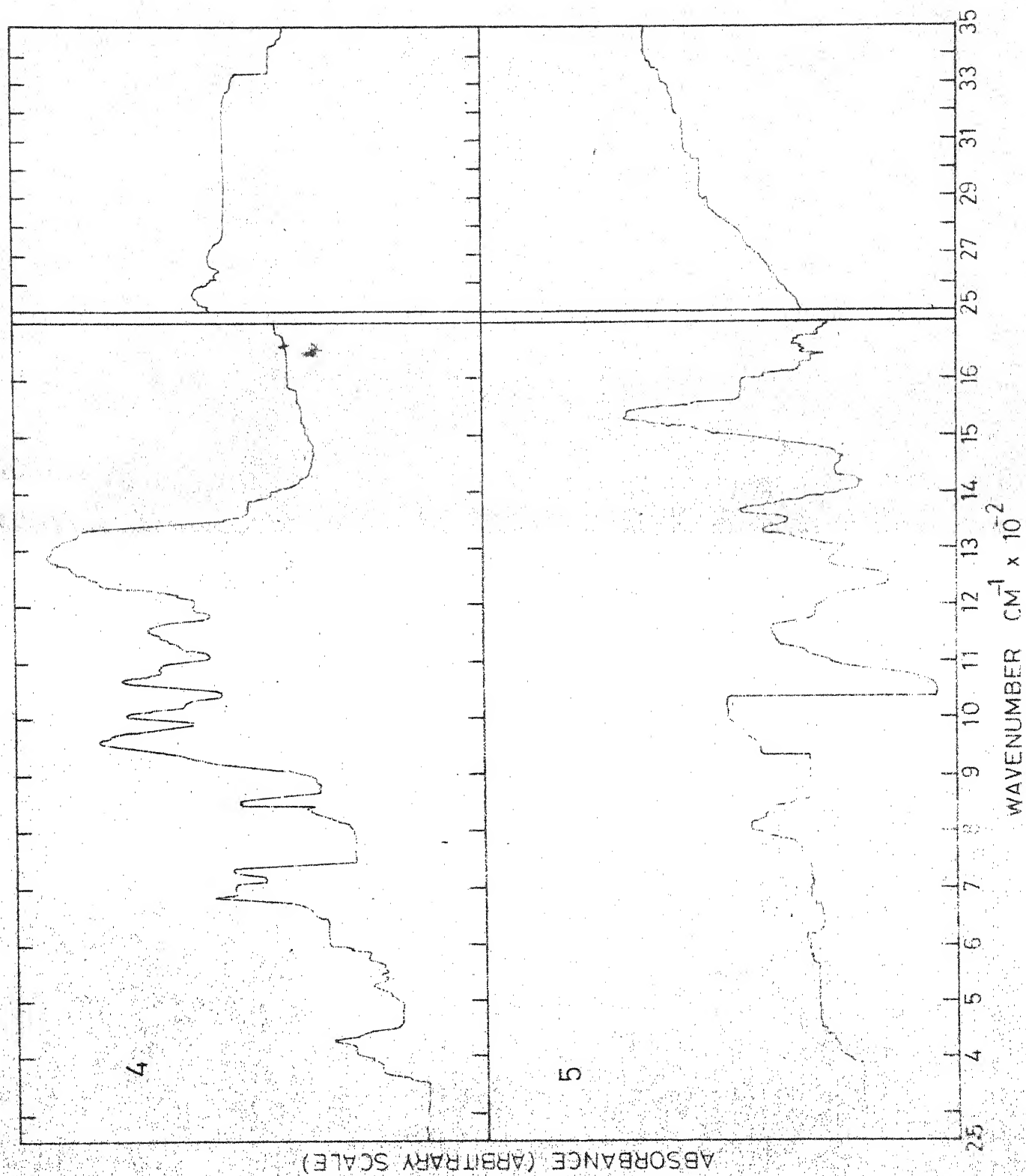


Fig. IV.1





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SECTION - B

CHAPTER V

CHELATING BEHAVIOUR OF 3,4,5-PYRIDAZINE TRITHIOL-I*
(Co(II), Cu(II), Ni(II), Fe(III), and Cr(III))

In this chapter, the preparations, the magnetic and the spectroscopic (i.r., u.v., visible) studies of the complexes of cobalt(II), nickel(II), copper(II), iron(III) and chromium(III) with 3,4,5-pyridazine trithiol have been reported. Based on them the probable structures of the complexes have been proposed.

EXPERIMENTAL

(A) Preparation of 3,4,5-Pyridazine Trithiol

3,4,5-Pyridazine trithiol $C_4H_4N_2S_3$ (hereafter referred to as TH_3) was prepared by the method given below:¹

* J. Inorg. & Nucl. Chem. (in Press) 1972.

4,5-Dichloro-3-pyridazone (2 g) was refluxed with 8 g of phosphorus pentasulphide in 150 ml of dry pyridine for sixteen hours. The mixture was kept overnight and vacuum distilled. The resulting product was dissolved in distilled water. The solution was filtered and the filtrate was acidified with concentrated hydrochloric acid, whereby a yellow precipitate of trithiol appeared. The precipitate was washed with water and dried, m.p. $>400^{\circ}\text{C}$.

(B) Preparation of Metal Complexes

(a) Bis(3,4,5-pyridazine trithiol)hexaaquo-cobalt(II).— 0.88 g sample of the ligand (~ 5 mmole) was dissolved in 200 ml of ethanol. To this a solution of 0.7 g of the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (~ 2.1 mmole) in 100 ml of ethanol was added slowly whereby a brown precipitate appeared. It was digested for about four hours on a water bath. The precipitate of the complex was filtered out and washed successively with water and ethanol. It was dried in an air oven at 120°C for a few hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Co}(\text{TH}_2)_2 \cdot 6\text{H}_2\text{O}$: C, 18.6; H, 3.5; N, 10.8; S, 37.1; Co, 11.4. Found: C, 18.2; H, 3.1; N, 10.4; S, 37.5; Co, 11.1.

(b) Mono(3,4,5-pyridazine-trithiol)nickel(II).— 0.43 g of the ligand (TH_3) (~ 2.4 mmole) was dissolved in 100 ml of ethanol and 0.6 g of the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (~ 2.5 mmole) in 100 ml of ethanol. The two solutions were mixed whereupon a brown precipitate appeared. It was digested for about five hours on a water bath. The precipitated complex was

filtered out, washed successively with hot distilled water and ethanol. It was dried in an air oven at 120°C for seven hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Ni}(\text{TH})$: C, 20.6; H, 0.9; N, 12.0; S, 41.2; Ni, 25.3. Found: C, 20.0; H, 1.2; N, 11.8; S, 41.7; Ni, 24.8.

(c) Tetrakis(3,4,5-pyridazine trithiol)decaaquopenta-copper(II).—

0.45 g of the ligand (TH_3) (~ 2.5 mmole) and 0.8 g of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (~ 4.7 mmole) were dissolved in 100 ml and 80 ml of ethanol respectively. The two solutions were mixed slowly whereby a greenish coloured precipitate appeared. It was stirred and kept overnight. The resulting precipitate was filtered, washed successively with water and ethanol. It was dried for a few hours in an air oven at 120°C , yielding a black coloured complex.

Anal. Calcd. for $\text{Cu}_5(\text{T})_2(\text{TH})_2 \cdot 10\text{H}_2\text{O}$: C, 16.1; H, 2.2; N, 9.4; S, 32.2; Cu, 26.6. Found: C, 16.4; H, 1.9; N, 9.7; S, 32.6; Cu, 26.1.

(d) Tris(3,4,5-pyridazine trithiol)triquoiron(III).— 0.90 g of the ligand (TH_3) (~ 5.1 mmole) was dissolved in 180 ml of ethanol and 0.3 g of hydrated ferric chloride (~ 1.8 mmole) was dissolved in 100 ml of ethanol. The two solutions were mixed whereupon a dark brown precipitate appeared. It was digested for about four hours on a water bath. The precipitate of the complex was filtered and washed successively with water and ethanol. It was dried in an air oven at 120°C for a few hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Fe}(\text{TH}_2)_3 \cdot 3\text{H}_2\text{O}$: C, 22.7; H, 2.4; N, 13.2; S, 45.4; Fe; 8.8. Found: C, 22.3; H, 2.3; N, 12.9; S, 45.0; Fe; 8.3.

(e) Mono(3,4,5-pyridazine trithiol)chromium(III).— 0.3 g sample of the ligand (TH_3) (~ 1.7 mmole) and 0.3 g of chromium chloride (CrCl_3) (~ 1.8 mmole) were dissolved in 60 ml and 50 ml respectively of ethanol. The two solutions were mixed and digested for about two hours on a water bath. The precipitate of the complex was filtered out and washed successively with water, ethanol and ether. It was dried in an air oven at 120°C for seven hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Cr}(\text{T})$: C, 21.3; H, 0.4; N, 12.4; S, 42.7; Cr, 23.1. Found: C, 20.9; H, 0.6; N, 12.2; S, 42.4; Cr, 22.8.

Analyses

The analyses of the metal ions and sulphur, were carried out by the standard methods.^{2,3} Carbon, hydrogen and nitrogen analyses were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur-16, India. The analytical results are given in the text.

Infrared Spectra.— Infrared spectra of the ligand and the complexes were recorded with a Perkin-Elmer Model 521 diffraction grating. Infrared Spectrophotometer in the range of $4000\text{--}250\text{ cm}^{-1}$. Samples were prepared as potassium bromide pellets. The major bands of

infrared spectra and their assignments are given in Table 1.

Magnetic Susceptibility Measurements.— Magnetic susceptibilities of these complexes were determined with the help of a Gouy balance at room temperature (27°C). Mercury tetrathiocyanato-cobaltate(II) was used as a magnetic susceptibility standard and the diamagnetic corrections were estimated by the method outlined by Figgis and Lewis.⁴ The results of magnetic moments of the complexes and their solubilities are given in Table II.

Visible Spectra.— The absorption spectra of the ligand and the complexes were recorded on a Cary-14 recording Spectrophotometer in nujol mull between 250 m μ and 1600 m μ .

RESULTS AND DISCUSSION

The empirical formulae of all the complexes are given in the text. Their molecular weights could not be determined due to complete insolubility in any organic or inorganic solvents. However, the complete insolubility in any of the solvents indicate the polymeric nature of these complexes. In these complexes the ligand can behave as mono-, bi-, tri-, tetra-, or pentadentate, depending upon the mode of linkage with the metal ion. Also the ligand can either act in the form of thione-thiol (X) or thiol form (II) as shown in figures of Chapter I.

The i.r. spectrum of the ligand has not been studied. Basically it contains three parts: (i) thioamide (H-N-C-S) group,

(ii) cis-dithiol group and (iii) N=N group. Therefore, its i.r. spectrum should show bands characteristic of thioamide group (4 bands)⁵, dithiol group (2 bands),^{6,7} N=N group.⁸ However, in such a delocalized system one can not expect pure bands due to such groups and therefore, the bands must be highly coupled. Besides the bands due to $\nu(\text{C-H})$, $\nu(\text{N-H})$, $\nu(\text{S-H})$, and other bending modes should also be present. Tentative assignments of the majority of the bands are given in Table 1.

The presence of the bands due to the $\nu(\text{N-H})$ group around 3100 cm^{-1} and due to $\nu(\text{S-H})$ group around 2400 cm^{-1} , suggests the ligand to be present in the thiol-thione form. It is quite possible that in solution, the ligand may be present in thiol form also due to thiol-thione tautomerism. However, we have assumed the ligand to be present in the thiol-thione form. Important changes in the positions and the intensities of various bands in the spectra of the complexes are as follows:

(a) The spectra of the cobalt, iron and copper complexes showed broad bands around 3450 cm^{-1} , and weak bands at 1600 cm^{-1} and 800 cm^{-1} . The positions of these bands suggest the presence of coordinated water molecules in the complex.⁹ The presence of coordinated water was also indicated by heating the complexes around 150°C , whereby the decrease in weight of the complexes corresponded to the same number of water molecules as given by analyses in the respective complexes (after heating, the complexes appeared to be decomposed).

Besides these bands, the moderately intense band around 3150 cm^{-1} and weak band around 2400 cm^{-1} were also present in their spectra. These bands suggest the presence of N-H and S-H groups in the complexes.

The spectrum of nickel complex showed a band at 3150 cm^{-1} , but no band around 2400 cm^{-1} . Similarly in the spectrum of the copper complex, there appeared no band at 3150 cm^{-1} and 2400 cm^{-1} . This indicated the presence of the N-H group in the nickel complex and the absence of both N-H and S-H groups in the copper complex.

(b) In the region $1550\text{ cm}^{-1} - 1450\text{ cm}^{-1}$, there appeared a band in the spectrum of the ligand which has been assigned to thioamide band(I) coupled with $\nu(\text{C}=\text{C})$. Similarly, another band around 1310 cm^{-1} is assigned to thioamide bands (II), coupled with $\nu(\text{C}=\text{C})$. In the spectra of complexes of nickel, cobalt, chromium and iron, the positions of these bands were not much shifted ($\pm 10\text{ cm}^{-1}$). It can, therefore, be inferred that possibly the N-H group is not used in bond formation. However, the positions of the thioamide bands (III) and (IV) around 1060 cm^{-1} and 815 cm^{-1} which might be coupled with $\nu(\text{C}-\text{N})$, and $\nu(\text{C}-\text{C})$ have been shifted to lower wave numbers. Since these bands contain major contribution from $\nu(\text{C}=\text{S})$, the bonding through thiocarbonyl sulphur has been assumed in these complexes.

In the spectrum of copper complex, the positions of all the four thioamide bands have been shifted to lower wave numbers, indicating the interaction of copper with both nitrogen (after deprotonation) and thiocarbonyl sulphur.

(c) The three characteristic "dithiene" bands^{6,7} (ω_1 , due to perturbed (C=C), ω_2 , ω_3 due to perturbed ν (C=S) can not be pure bands, but must be coupled with other modes of vibration of the ligand, e.g., ν (C=N), ν (N=N), ν (C-N), and ν (C=S) of the thioamide group etc. In the spectrum of the ligand, the ω_2 band was not observed, but the spectrum of its sodium salt shows two bands at 1160 cm^{-1} and 1100 cm^{-1} . Similar bands around the same positions appeared in all the complexes. These bands in the spectra of the sodium salt and the complexes are assigned to ω_2 band of the dithiene group. All the three characteristic "dithiene" bands are split ones. The splitting may be due to the inter-molecular interactions. In the spectra of all the complexes, the positions of the ω_3 bands were shifted to lower wave number as compared to that of the ligand in the hydrogen form. This indicates that there is definite interaction of thiol sulphur atoms with the metal ion. As usual the frequencies at which the dithiene bands appeared did not change with the metal ions and remained almost invariant.¹⁰

(d) The bands in the spectrum of copper complex were broad. One may, therefore, tentatively infer that the copper complex is highly polymeric in nature.

(e) New bands appeared in the spectra of all the complexes around 350 cm^{-1} . These bands are assigned to ν (M-S) vibrations.¹⁰ Generally in the spectra of the dithiolene complexes, these bands appear

around 400 cm^{-1} (ω_4) and 350 cm^{-1} (ω_5). Since the spectra were quite complex in the region of 400 cm^{-1} , the 400 cm^{-1} band (ω_4) could not be identified.

Magnetic Moments and Visible Spectra

The values of the magnetic moments of the various complexes are given in Table II. These values are much lower than the spin only values. This suggests that in all these complexes, there is metal-metal interaction such that the spins of the various electrons are paired.

The absorption spectrum of the ligand in nujol mull showed continuous absorption from $1600\text{ m}\mu$ to $500\text{ m}\mu$. Between $500\text{ m}\mu$ and $250\text{ m}\mu$, three bands were observed at 500 , 410 and $340\text{ m}\mu$. These bands may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the thio-carbonyl and thiol groups. In the spectra of the complexes, there was continuous absorption from $1500\text{ m}\mu$ to $550\text{ m}\mu$ and these three bands in the region $500\text{ m}\mu$ - $300\text{ m}\mu$, were slightly shifted towards shorter wave lengths. Besides these bands, there also appeared some shoulders which may be assigned to d-d transitions. The spectrum of the nickel complex had two shoulders at $740\text{ m}\mu$ and $610\text{ m}\mu$. If a distorted octahedral geometry is assumed around nickel ion, one should expect a band in this region due to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transition. In a distorted octahedral field, T_{1g} term gets split, thereby producing two or three bands respectively. This band should not split in a tetrahedral field due to the non-degenerate nature of A_{2g} . The magnetic moment of

nickel complex is 1.69 B.M., indicating one unpaired electron per nickel atom. Thus, tentatively one can assign structure I' to the nickel complex.

In the spectrum of copper complex, there was only one broad band with a maximum at 550 $m\mu$. The band at 410 $m\mu$ and 340 $m\mu$ appeared only as shoulders. The bands at 550 $m\mu$ is characteristic of octahedral complex. However, owing to Jahn Teller effect an octahedron can not be regular. There might appear other weak bands due to lowering of the symmetry. But these bands did not appear in the spectrum due to the presence of charge transfer bands. The band at 340 $m\mu$ has been intensified and slightly broadened. Tsuchida, et al.,¹¹⁻¹³ indicated that all the copper complexes having metal to metal interaction absorb in the 375 $m\mu$ region. Therefore, the intensification and broadening of the 340 $m\mu$ band may be due to the presence of intense band in this region, due to copper-copper linkage. The metal-metal bond is also indicated by the magnetic susceptibility data.

The magnetic moment of the complex is 0.45 B.M., indicating partial quenching of the magnetic moment. The quenching may be due to direct metal to metal linkage or through super-exchange mechanism. It is not possible however, to prefer either of the two mechanisms in this case.

Based on these observations, structure II has been proposed for the complex.

The magnetic moment of cobalt(II) and iron(III) complexes are quite surprising. The values for cobalt and iron suggest that the metal ion has dsp^3 or dsp^2 type of bonding giving the complexes a pyramidal or square-planar geometry. Their spectra do not show any definite bands which can throw some light on their stereochemistry.

The magnetic moment of chromium(III) complex is very interesting. The value is much below even for one unpaired electron. How the spin interaction takes place can not be explained. The spectrum (u.v. & visible) indicates only one broad band at $700\text{ m}\mu$ (Half width = 400 cm^{-1}) and therefore, no definite or tentative structure could be assigned to the complex.

Table I

Assignments of the Major Infrared Bands of the Ligand,
Sodium Salt of the Ligand and the Complexes (cm^{-1})

Ligand	Sodium salt of the ligand	Complexes	Assignments
-	-	3450 ^a (B)	$\nu(\text{OH})$
3130	-	3180 ^b	$\nu(\text{N-H})$ group
3080	-	-	Fermi resonance
2400	-	2400 ^c (V.W)	$\nu(\text{S-H})$
-	-	1600 ^a	(O-H) in plane bending mode
1520(B) (splitted)	1490	1500(B) (splitted)	Thioamide band I ^d + $\nu(\text{C}=\text{C})$ + $\nu(\text{N}=\text{N})$
1455(W)	1455(W)	1455(W)(± 10)	$\nu(\text{N}=\text{N})$ + $\nu(\text{C}=\text{C})$
1365 (splitted)	1365	1325(± 20)	Thioamide band II ^e + $\nu(\text{C}=\text{C})$ ^f
-	1160 1100	1150) 1100)(± 10)	$\nu(\text{C-N})$
1060	1015	1038(± 10)	Thioamide band III ^g
970,940, 920,900	895,860, 840	885,850,840(± 10)	$\nu(\text{C-S})$ ^h
-	-	800 ^a	$\delta(\text{O-H})$
815	800	800 \pm 20	Thioamide band IV ⁱ
760	760	~ 760	(C-H) out of plane
-	-	~ 350	$\nu(\text{M-S})$ ^j

a) Present in all complexes except those of Ni(II) and Cr(III); b) Present in Co(II), Fe(III) and Ni(II) complexes; c) Present in Co(II) and Fe(III) complexes; d) Due to $\delta(\text{N-H})$ + $\nu(\text{C-N})$; e) Mainly due to $\nu(\text{C-N})$ and $\nu(\text{C=S})$; f) Characteristic band ω_1 of cis-dithiol group; g) Mainly due to $\nu(\text{C-N})$ + $\nu(\text{C=S})$; h) Characteristic band ω_2 of cis-dithiol group + $\nu(\text{C=S})$ of thioamide group; i) Mainly due to $\nu(\text{C=S})$; j) The positions of these bands varies with the metal ions.

Table II

Solubilities and the Magnetic Moments of the Complexes

Complexes	$\mu_{\text{eff.}}$ B.M.	Solubility
(a) Bis(3,4,5-pyridazine trithiol)- hexaaquo-cobalt(II). $\text{Co}(\text{TH}_2)_2 \cdot 6\text{H}_2\text{O}$	2.7	I
(b) Mono(3,4,5-pyridazine trithiol)- nickel(II). $\text{Ni}(\text{TH})$	1.6	I
(c) Tetrakis(3,4,5-pyridazine trithiol)- decaquo-pentacopper(II). $\text{Cu}_5(\text{T})_2(\text{TH})_2 \cdot 10\text{H}_2\text{O}$	0.7	I
(d) Tris(3,4,5-pyridazine trithiol)- triaquo-iron(III). $\text{Fe}(\text{TH}_2)_3 \cdot 3\text{H}_2\text{O}$	4.4	I
(e) Mono(3,4,5-pyridazine trithiol)- chromium(III). $\text{Cr}(\text{T})$	0.7	I

I) Insoluble in chloroform, carbon-tetrachloride, benzene, tetrahydrofurane, cyclohexane, xylene, toluene, acetone, methanol, dioxane, dichloro-ethane and dichloro-methane.

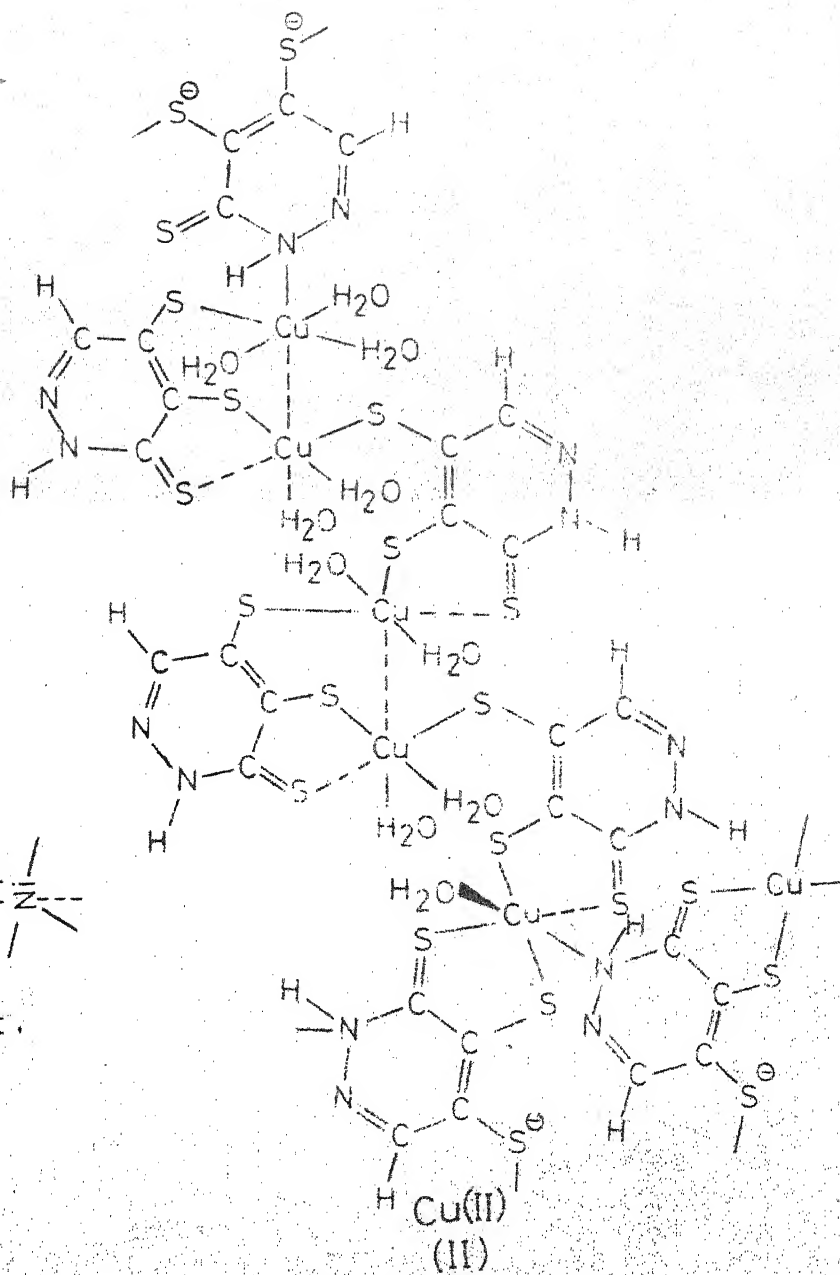
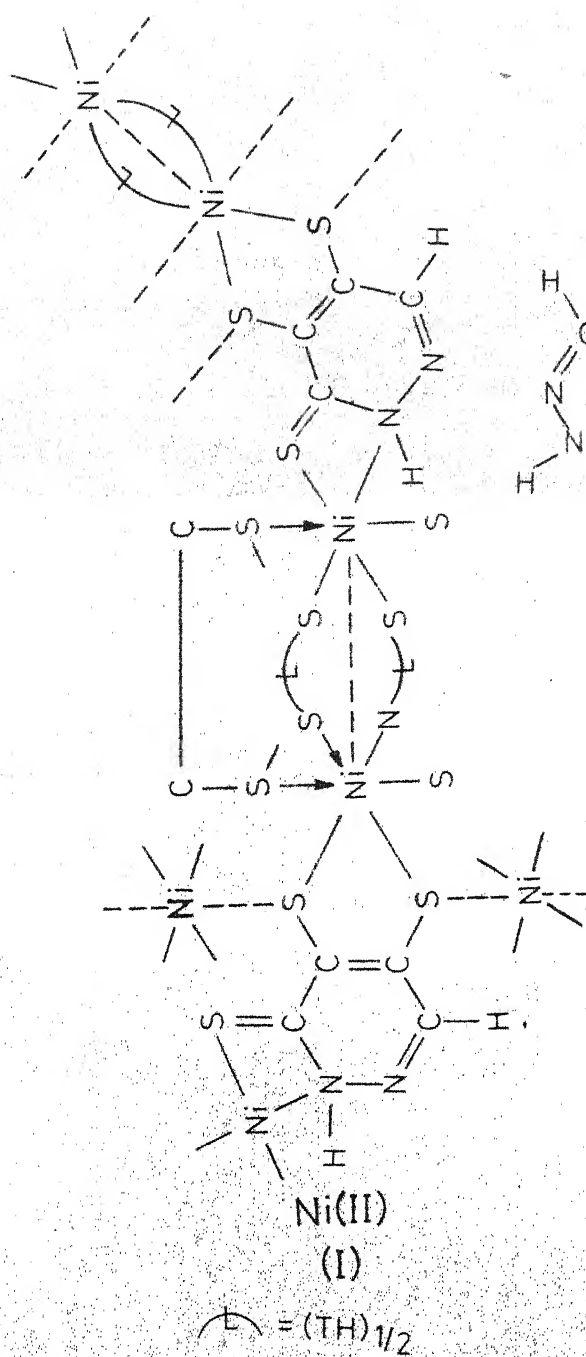


Fig. V.1

1. 3,4,5-Pyridazine trithiol
2. Sodium salt of 3,4,5-Pyridazine trithiol
3. $\text{Co}(\text{TH}_2)_2 \cdot 6\text{H}_2\text{O}$
4. $\text{Ni}(\text{TH})$
5. $\text{Cu}_5(\text{T})_2(\text{TH})_2 \cdot 10\text{H}_2\text{O}$
6. $\text{Fe}(\text{TH}_2)_3 \cdot 3\text{H}_2\text{O}$
7. $\text{Cr}(\text{T})$.

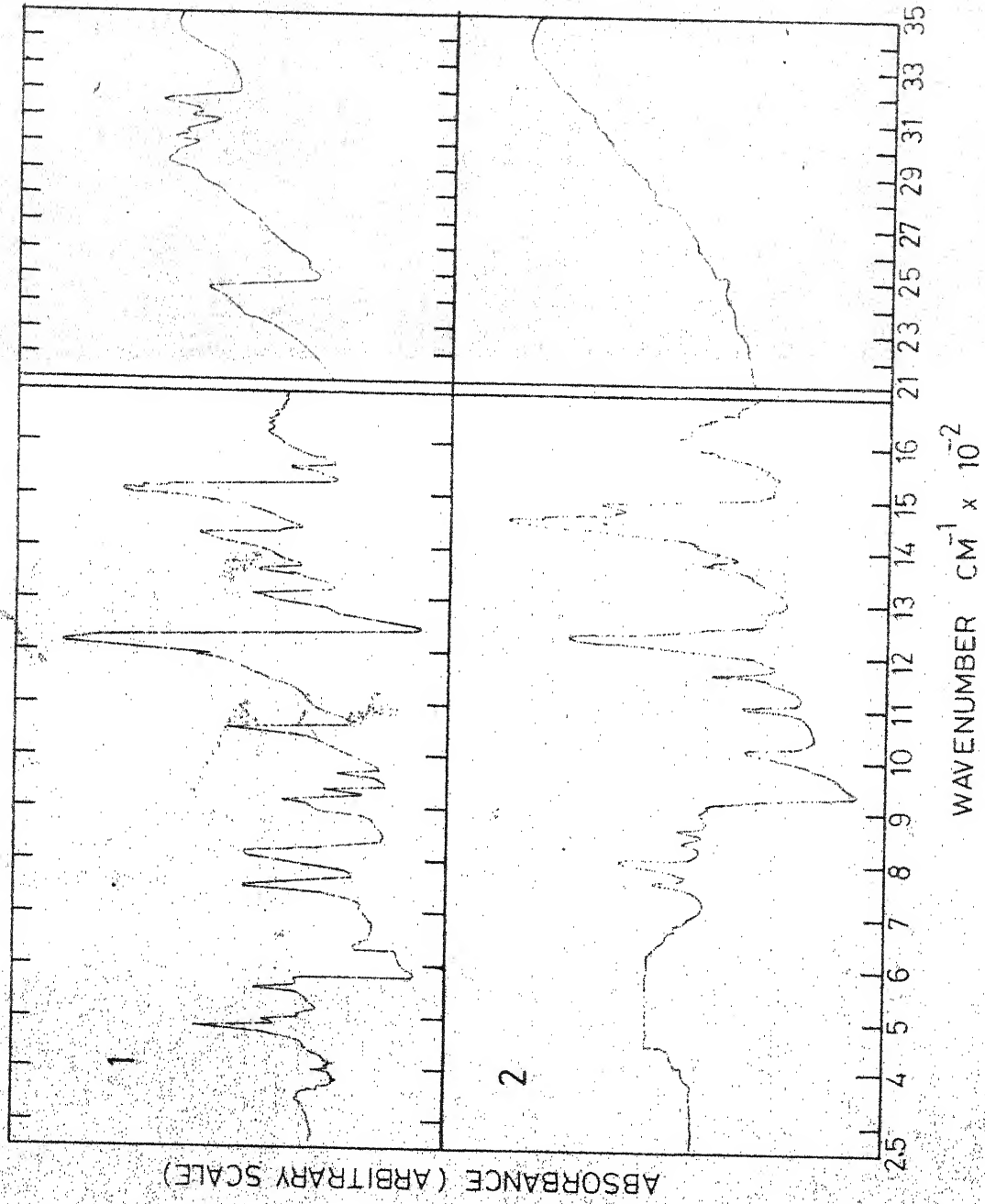


Fig. V.1

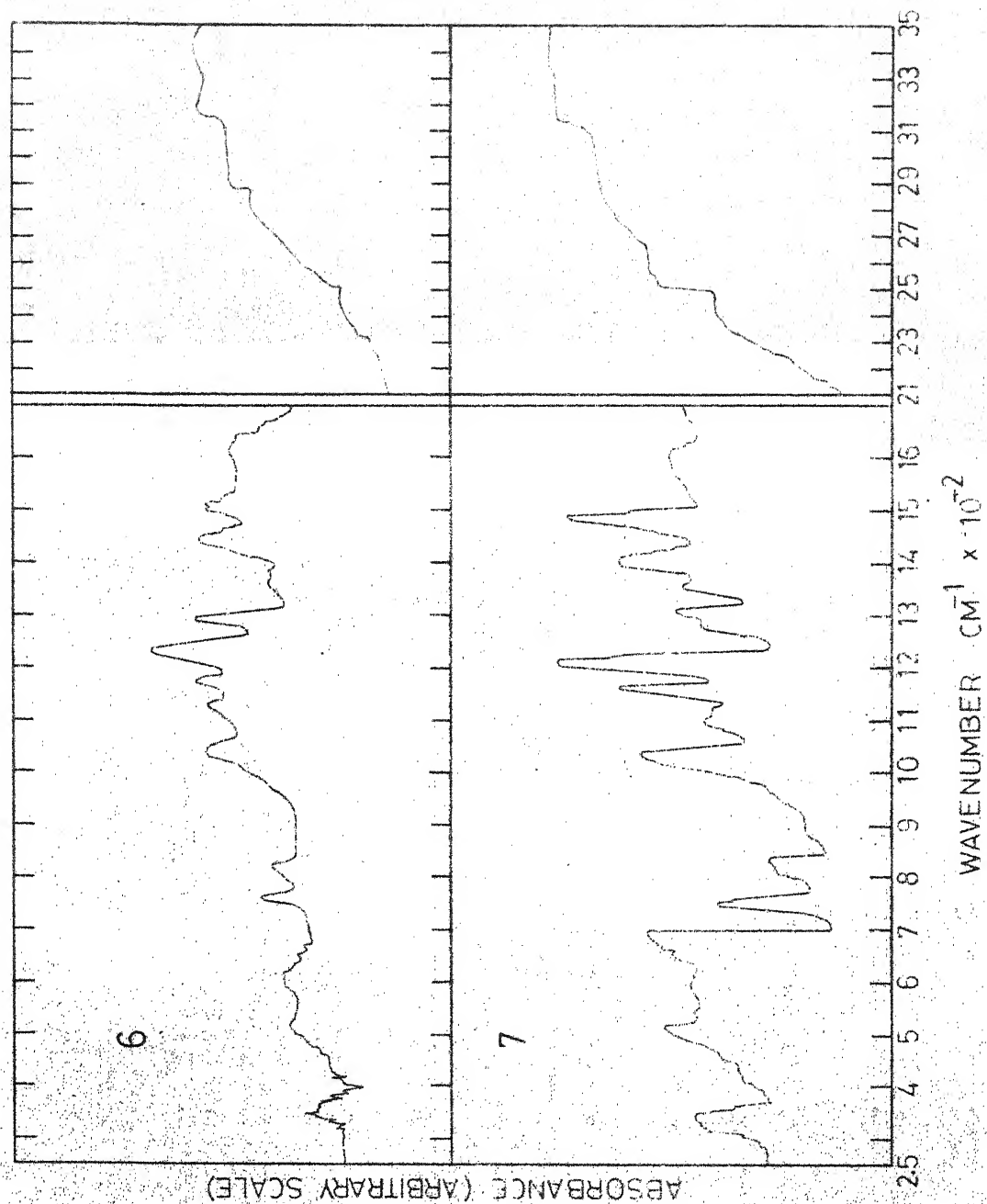


Fig. V.1

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CHAPTER VI

CHELATING BEHAVIOUR OF 3,4,5-PYRIDAZINE TRITHIOL-II*

(Pd(0), Pd(II), Rh(I), Rh(II), Rh(III),
Ru(II), Ru(III), Pt(II) and Pt(IV))

In this chapter the preparations of the complexes with palladium(0); palladium(II); rhodium(I); rhodium(II); rhodium(III); ruthenium(II); ruthenium(III); platinum(II) and platinum(IV) with 3,4,5-pyridazine trithiol are reported. The infrared and visible spectra, and the magnetic moments of the complexes have been studied. Based on these studies structures have been proposed for the complexes.

EXPERIMENTAL

(A) Preparation of 3,4,5-Pyridazine Trithiol

3,4,5-Pyridazine trithiol $C_4H_4N_2S_3$ (hereafter referred to as TH_3), was prepared by the method given in Chapter V.

* Communicated to Inorg. Chem. (1972).

(B) Preparation of Metal Complexes(a) Mono(3,4,5-pyridazine trithiol)mono(triphenylphosphine)palladium(0).--

Tetrakis(triphenylphosphine)palladium(0) was prepared by the published procedure.¹ 0.40 g of the $\text{Pd}(\text{P}\phi_3)_4$ (~ 0.34 mmole) was dissolved in 70 ml of ethanol at about 70°C . To this, 0.4 g of the ligand (TH_3) (~ 2.3 mmole) in 100 ml of ethanol was added dropwise, whereby a buff coloured precipitate appeared. The mixture was digested on a water bath at about 80°C for ten minutes and kept overnight at room temperature. The precipitated complex was centrifuged and washed successively with hot ethanol, water and finally with ether. It was dried in a vacuum desiccator for about eight hours at room temperature, yielding a buff coloured complex.

Anal. Calcd. for $\text{Pd}(\text{TH}_3)\text{P}\phi_3$: C, 48.5; H, 3.5; N, 5.1; S, 17.7; Pd, 19.5. Found: C, 48.2; H, 3.3; N, 4.9; S, 17.3; Pd, 19.1.

(b) Tris(3,4,5-pyridazine trithiol)dipalladium(II).-- 0.45 g of the ligand (TH_3) (~ 2.5 mmole) was dissolved in 100 ml of ethanol and 0.3 g of PdCl_2 (~ 1.6 mmole) was dissolved in very dilute hydrochloric acid. The two solutions were mixed and digested on a waterbath for about four hours. The precipitate of the complex was filtered out, washed successively with water and ethanol. It was dried in an air oven at 120°C for ten hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Pd}_2(\text{TH})_2(\text{TH}_3)$: C, 19.5; H, 1.1; N, 11.4; S, 39.1; Pd, 28.9. Found: C, 19.4; H, 0.9; N, 10.9; S, 39.5; Pd, 28.4.

(c) Tris(3,4,5-pyridazine trithiol)monochloro-rhodium(I).— Tris(tri-phenylphosphine)monochloro-rhodium(I) was prepared by the known procedure.² A solution of 0.3 g of the $\text{Rh}(\text{P}\phi_3)_3\text{Cl}$ (~ 0.3 mmole) was prepared in 40 ml of benzene. To this, a solution of 0.90 g of the ligand (TH_3) (~ 5.6 mmole) in 190 ml of ethanol was added dropwise. The mixture was heated on a water bath at about 80°C for seven hours and the precipitated complex was filtered out and washed successively with hot benzene, ethanol and finally with ether. It was dried in an air oven at 120°C for about six hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Rh}(\text{TH}_3)_3\text{Cl}$: C, 21.6; H, 1.8; N, 12.6; S, 43.2; Rh, 15.5; Cl, 5.3. Found: C, 21.4; H, 1.3; N, 12.4; S, 43.6; Rh, 15.1; Cl, 4.9.

(d) Tetrakis(3,4,5-pyridazine trithiol)di-aquodirrhodium(II).— $[\text{Rh}(\text{II})(\text{CCl}_3\text{COO})_2]_2$ complex was prepared by a slightly modified Winkhaus and Zeigler method.³ The greenish blue crystals, thus obtained, were dissolved in about 50 ml of ethanol at room temperature. The resulting solution was mixed with a solution of 0.30 g of the ligand (TH_3) (~ 1.7 mmole) in 60 ml of ethanol and digested on a water bath at $60-70^\circ\text{C}$ for about two hours. The precipitated complex was filtered out and washed successively with boiling ethanol and ether. It was dried in an air oven at 120°C overnight, yielding a brown coloured complex.

Anal. Calcd. for $[\text{Rh}(\text{TH}_2)_2\text{H}_2\text{O}]_2$: C, 20.4; H, 1.7; N, 11.9; S, 40.8; Rh, 21.9. Found: C, 20.3; H, 1.2; N, 12.3; S, 40.4; Rh, 21.4.

(e) Tris(3,4,5-pyridazine trithiol)dirhodium(III).— 0.45 g of the ligand (TH_3) (~ 2.5 mmole) and 0.3 g of RhCl_3 (~ 1.1 mmole) were dissolved in 100 ml and 70 ml of ethanol respectively. The two solutions were mixed slowly and digested on a water bath for about three hours. The precipitate of the complex thus obtained was filtered out and washed successively with hot distilled water and ethanol. It was dried in an air oven at 120°C for six hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Rh}_2(\text{TH})_3$: C, 19.8; H, 0.8; N, 11.5; S, 39.6; Rh, 28.3. Found: C, 20.0; H, 1.2; N, 11.3; S, 39.4; Rh, 28.7.

(f) Tris(3,4,5-pyridazine trithiol)hexaquo-diruthenium(II).— The Ru(II) complex $(\text{Ru}_5\text{Cl}_{12})^{-2}$ was first obtained as a deep blue species by Wilkinson, et al. method.⁴ To this deep blue solution 0.4 g of the ligand (TH_3) (~ 2.3 mmole) in 80 ml of ethanol was added. The mixture was refluxed for four hours. The resulting precipitate of the complex was filtered out and washed successively with hot water, ethanol and finally with ether. It was dried in an air oven at 120°C for ten hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Ru}_2(\text{TH})(\text{TH}_2)_2 \cdot 6\text{H}_2\text{O}$: C, 17.3; H, 2.4; N, 10.1; S, 34.5; Ru, 24.4. Found: C, 17.5; H, 2.9; N, 10.4; S, 34.1; Ru, 24.8.

(g) Mono(3,4,5-pyridazine trithiol)monochloro-monoaquoruthenium(III).— 0.3 g of the ligand (TH_3) (~ 1.7 mmole) was dissolved in 60 ml of ethanol and 0.3 g of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (~ 0.9 mmole) was dissolved in 120 ml of ethanol. The two solutions were mixed and digested for about three hours on a water bath. The precipitate of the complex was filtered out, washed successively with hot water and ethanol. It was dried in an air oven at 120°C for about eight hours, yielding a brown coloured complex.

Anal. Calcd. for $\text{Ru}(\text{TH})\text{Cl} \cdot \text{H}_2\text{O}$: C, 14.6; H, 1.2; N, 8.4; S, 29.3; Ru, 30.8; Cl, 10.7. Found: C, 15.0; H, 0.9; N, 8.7; S, 28.9; Ru, 30.3; Cl, 11.1.

(h) Tris(3,4,5-pyridazine trithiol)diplatinum(II).— 0.35 g sample of the ligand (TH_3) (~ 1.9 mmole) was dissolved in 70 ml of ethanol and 0.2 g (~ 0.3 mmole) of the K_2PtCl_4 was dissolved in 25 ml of distilled water. The two solutions were mixed whereby a red coloured precipitate appeared. It was digested for about two hours on a water bath. The precipitate of the complex was centrifuged and washed successively with hot water, ethanol and finally with ether. It was dried in an air oven at 120°C for four hours, yielding a black coloured complex.

Anal. Calcd. for $\text{Pt}_2(\text{TH})_2(\text{TH}_3)$: C, 15.8; H, 0.9; N, 9.2; S, 31.5; Pt, 42.7. Found: C, 15.5; H, 1.2; N, 9.5; S, 31.8; Pt, 42.2.

(i) Bis(3,4,5-pyridazine trithiol)platinum(IV).-- 0.5 g of the ligand (TH_3) (~ 2.8 mmole) was dissolved in 100 ml of ethanol and 0.25 g of the K_2PtCl_6 (~ 0.36 mmole) in very dilute hydrochloric acid. The two solutions were mixed, whereby a black coloured precipitate was obtained. It was digested for about one hour on a water bath. The precipitate of the complex was centrifuged and washed successively with hot water, ethanol and finally with ether. It was dried in an air oven at 120°C for six hours, yielding a black coloured complex.

Anal. Calcd. for $\text{Pt}(\text{TH})_2$: C, 17.7; H, 0.7; N, 10.3; S, 35.4; Pt, 35.9. Found: C, 17.4; H, 1.1; N, 10.1; S, 34.9; Pt, 35.6.

Oxidation State of Metal Ions

The oxidation states of the metal ions, Rh(I) and Rh(II) were determined by the procedure described in the literature.⁵ Rh(I) titrated for two electron change and Rh(II) for one electron change.

The oxidation state of palladium in $\text{Pd}(\text{TH}_3)\text{P}\phi_3$ complex was carried out according to the method given by Malatesta.⁶ It indicated two electron change per mole of the complex in the reaction.

(The exact procedure for the determination of the oxidation states of the metal ions Rh(I), Rh(II) and Pd(0) complexes are given in Chapter IV of the thesis).

Methods and Techniques

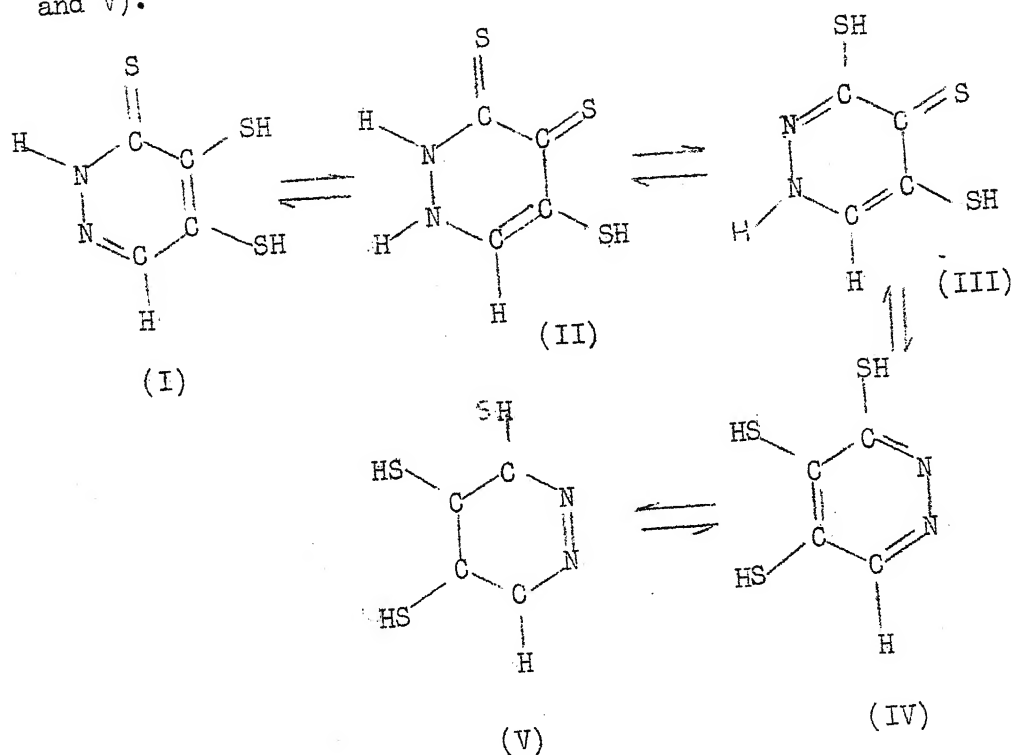
The analyses of the metal ions, chloride and sulphur were carried out by the standard methods given in the literature.^{7,8} Carbon, hydrogen, and nitrogen analyses were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur-16, India. The analytical results are given in the text. The infrared spectra, magnetic susceptibility measurements and visible spectra of the complexes and the ligand (TH_3) have been taken by the same method as given in Chapter V of the thesis. The major bands of the infrared spectra and their assignments are given in Table I. The results of the magnetic moment of the complexes and their solubilities are given in Table II.

RESULTS AND DISCUSSION

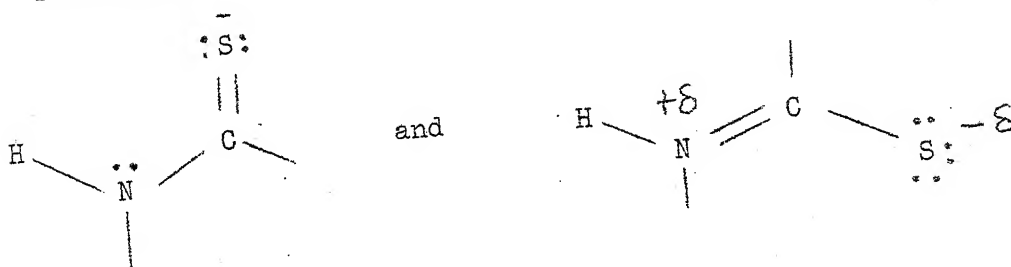
Palladium(0) and Rhodium(I) Complexes

The analytical data of these complexes (given in the text) suggest their formulae to be $\text{Pd}(\text{TH}_3)\text{P}\phi_3$ and $\text{Rh}(\text{TH}_3)_3\text{Cl}$. The respective oxidation states of the metals in the complexes were verified by the oxidation reduction titration which showed two electron change per mole of the complex. Most of the complexes of palladium(0) with coordination number of four have been shown the tetrahedral geometry and those of rhodium(I), the square planar geometry.⁹ Assuming these geometries and the oxidation states, the ligand in these complexes must behave as tridentate. The ligand molecule has five positions (two nitrogen

and three sulphur atoms) where the coordination with metal can take place. Out of these five positions, it is possible to choose tentatively three positions by the i.r. spectral studies. The ligand can exist in the following five tautomeric forms (I, II, III, IV and V).



Besides these, structures (I) and (II) can also be represented by the following resonance structures:



This type of resonance is not possible in structures (III), (IV) and (V). Therefore, if the bonding of the metal atom is through thiocarbonyl sulphur, the positions of the bands having major contributions from the bonds (C=S) and (N-H) should move towards higher wave numbers, while those having the major contribution from C=C bond should go down. In the spectra of Pd(O) and Rh(I) the positions of ν (N-H) ($\sim 20 \text{ cm}^{-1}$) and that of the thioamide bands (III) and (IV) ($\sim 30 \text{ cm}^{-1}$) shifted towards higher wave numbers, while the positions of the thioamide bands (I) and (II) are shifted towards lower wave numbers ($\sim 15 \text{ cm}^{-1}$). The characteristic thiol band¹⁰ (ω_1) is also shifted towards lower wave number. Bonding through thiol sulphur atoms, will shift the positions of ν (C-S) and ν (S-H) towards lower wave numbers. The characteristic dithiol bands (ω_2) shifted to around 790 cm^{-1} and 810 cm^{-1} in palladium(O) and Rh(I) complexes respectively, indicating metal to thiol sulphur bonding.

Thus it appears from the i.r. spectral data that the bonds in these complexes are through thiol and thione sulphur atoms and not through nitrogen atom. Also these elements being classified as class 'b' type¹¹ always prefer to form bonds with more polarizable atoms like sulphur.

Both the complexes are diamagnetic indicating the singlet ground state, which one should expect if one assumes the preferred arrangements of the ligands around the metals atoms Pd(O), tetrahedral, and Rh(I), square planar.

The spectrum of Pd(0) in the visible region did not show any d-d transition bands. It is quite similar to that of the ligand ^{that} except the bands in the complex are shifted slightly towards shorter wave length side. In the reflectance spectrum of the Rh(I) complex, there are two bands at $12,900\text{ cm}^{-1}$ and $16,700\text{ cm}^{-1}$ with relative intensities 1:3. The band at $12,900\text{ cm}^{-1}$ is broad and very weak, while the one at $16,700\text{ cm}^{-1}$ is weak or medium intense. Several workers have given the energy level scheme of the d^8 system for a square planar arrangement to explain the spectra of Pd(II) and Pt(II) complexes,¹²⁻¹⁵ but no assignments have yet been made of the electronic spectral bands of square-planar Rh(I) complexes. But they all show a band in the region $20,000\text{ cm}^{-1}$.⁵ Tentatively we assign the $12,900\text{ cm}^{-1}$ band to the spin forbidden transition $^1A_{1g} \longrightarrow ^3A_{2g}$ and the band at $16,700\text{ cm}^{-1}$ to either spin forbidden transition $^1A_{1g} \longrightarrow ^3B_{1g}$ or the spin allowed transition $^1A_{1g} \longrightarrow ^1B_{1g}$. But the relatively intense absorption suggests it to be the singlet-singlet transition.

On the basis of the above studies structures VI and VII can be tentatively assigned to Pd(0) and Rh(I) complexes respectively.

Platinum(II) and Palladium(II) Complexes

Both complexes have the same stereochemical composition $M_2(TH)_2(TH_3)$. The complexes of these elements always prefer to have the square-planar geometry.

The i.r. spectra of these complexes show the following changes as compared to that of the ligand: (i) The bands due to ν (N-H), thioamide bands I, II, III and IV and the characteristic bands of cis-dithiol groups $\omega_1\omega_2$ were split and among the split bands, one of the two or more bands arising due to splitting of the original ligand band corresponds with those positions found in the spectra of the Pd(0) or Rh(I) complexes i.e. ν (N-H), thioamide bands (III) and (IV) etc, shifted to higher wave number and thioamide band (I), (II) and ν (C-S) position shifted to lower wave numbers, indicating the bonding through thiocarbonyl sulphur atom. The remaining bands correspond to those found in the spectra of those complexes in which the metal ions are attached to thiol sulphur only. It indicates that in the complexes of Pt(II) and Pd(II), the ligand molecules are attached in two ways: (a) one ligand molecule is acting as tridentate and (b) the other molecule is acting as bidentate among the two platinum atoms. (ii) The bands due to ν (S-H) group are present around 2400 cm^{-1} , but the intensity goes down, indicating that all the (S-H) groups are not deprotonated.

These complexes are diamagnetic indicating the singlet ground state and also the preferred square-planar geometry of the complexes.

The reflectance spectrum of palladium(II) complex shows only one broad band at $20,050\text{ cm}^{-1}$ and that of platinum(II), shows two broad bands at $16,130\text{ cm}^{-1}$ and $30,000\text{ cm}^{-1}$ with relative absorbance 1:4. The long wave length side band in the case of palladium is not observed

due to the presence of intense charge transfer bands in that region of the spectrum. We assign tentatively the high energy bands at $20,050\text{ cm}^{-1}$ and $30,000\text{ cm}^{-1}$ in palladium and platinum complexes due to singlet-singlet transition, $^1A_{1g} \rightarrow ^1B_{1g}$ and the low energy band at $16,130\text{ cm}^{-1}$ in platinum complex due to singlet-triplet transition. $^1A_{1g} \rightarrow ^3A_{2g}$. It is interesting to note that the order in which spin allowed bands in rhodium(I), palladium(II) and platinum(II) complexes (all d^8 systems) appeared is $\text{Rh(I)} < \text{Pd(II)} < \text{Pt(II)}$.

The order is the same as that of the increase in Dq value in going from lower to higher charge ($\text{Rh(I)} < \text{Pd(II)}$) and also in going from the second transition series to third transition series ($\text{Pd(II)} < \text{Pt(II)}$). Similar order in the shift is observed in the singlet \rightarrow triplet transition also. Thus the visible spectra of these complexes indicate the square-planar geometry. Therefore, we tentatively assign structure (VIII) to both the complexes.

Rhodium(III), Ruthenium(II) and Platinum(IV) Complexes

The analytical data of these complexes suggest their formulae to be $\text{Rh}_2(\text{TH})_3$, $\text{Pt}(\text{TH})_2$ and $\text{Ru}_2(\text{TH})(\text{TH}_2)_2 \cdot 6\text{H}_2\text{O}$. The water content in ruthenium(II) complex was verified by the decrease in weight on heating the complex at 150°C , which corresponded to three water molecules per ruthenium atom. All the three metal ions in these complexes prefer to have octahedral geometry.⁹

The i.r. spectrum of ruthenium(II) complex is similar to those of palladium(II) and platinum(II) complexes, except that there are

three extra prominent bands in the ruthenium complex due to water molecules at 3400 cm^{-1} (B), 1620 cm^{-1} (W.B) and 880 cm^{-1} (V.B). This indicates that the bonding in ruthenium complex is similar to those in Pt(II) and Pd(II) complexes.

The vibrational spectrum of platinum(IV) compares well with those of palladium(0) and rhodium(I). The major differences among them are the following: (i) ν (S-H) bands present in the spectra of Pd(0) and Rh(I) complexes, disappeared in Pt(IV) complex; (ii) the intensities of the bands containing a large contribution from ν (C-N) at 1040 cm^{-1} (thioamide band (III)), 1170 cm^{-1} and 1110 cm^{-1} were relatively high in the spectrum of the Pt(IV) complex; (iii) the position of the cis-dithiol band(II) (ω_2) shifted relatively too much lower wave numbers. Its intensity, and that of thioamide band (IV) also went down in platinum (IV) complex, indicating more of thiol character of the ligand in the complex. One of the possible explanations for these differences may be that due to very high charge on the metal ion, platinum(IV) could polarize the thione-sulphur atom besides thiol sulphur atom and the contribution from the resonance structure $\text{H}-\overset{+}{\text{N}}=\overset{+}{\text{C}}-\overset{-}{\text{S}}:$ of tautomeric structures (I) and (II) becomes high. This will tend to raise the intensities of the bands having ν (C-N) contribution and lower down the intensities of those bands containing contribution from ν (C=S). Thus, it appears from the i.r. spectrum that the ligand in the platinum(IV) complex is behaving as tridentate and is linked to sulphur atoms.

The spectrum of rhodium(III) complex, shows most of the bands as broad ones. However, their positions are the expected ones. The spectrum showed bands due to $\nu(\text{S-H})$, $\nu(\text{N-H})$ groups, indicating the presence of these bands in all or a few of the ligand molecules.

The complexes are diamagnetic, indicating them in singlet ground state. The diamagnetism in these complexes also suggests the octahedral geometries of these complexes.

The visible spectrum of ruthenium(II) complex showed a weak band at $14,700\text{ cm}^{-1}$ and those of Rh(III) and Pt(IV) complexes at $20,000\text{ cm}^{-1}$ and $24,000\text{ cm}^{-1}$ respectively. In the spectrum of Pt(IV) complex, there is another very weak band at $17,500\text{ cm}^{-1}$ and a medium intense band at $30,000\text{ cm}^{-1}$ having the same intensity as that at $24,000\text{ cm}^{-1}$. The position of the bands in Ru(II) and Rh(III) complexes are the same as one would expect for the complexes having the octahedral geometries.¹⁶ These bands may be due to singlet-singlet transition $^1A_{1g} \rightarrow ^1T_{1g}$. The bands in the Pt(IV) complex are assigned as follows: $17,500\text{ cm}^{-1}$ to $^1A_{1g} \rightarrow ^3T_{1g}$; $24,000\text{ cm}^{-1}$ to $^1A_{1g} \rightarrow ^1T_{1g}$ and the one at $30,000\text{ cm}^{-1}$ to $^1A_{1g} \rightarrow ^1T_{2g}$. The positions of these bands correspond very well with the other octahedral complexes of Pt(IV).¹⁶ Using these transitions, the values for $10 Dq$, F_2 and F_4 are calculated to be $27,265\text{ cm}^{-1}$, 840 cm^{-1} and 93 cm^{-1} respectively. These are within the range for the Pt(IV) octahedral complexes.

Thus on the basis of i.r., visible spectral and magnetic moment data, the structures IX, X and XI are tentatively assigned for the complexes.

Rhodium(II) and Ruthenium(III) Complexes:

The analytical data of these complexes predicted their formulae as $(\text{Rh}(\text{TH}_2)_2 \cdot \text{H}_2\text{O})_2$ and $\text{Ru}(\text{TH})\text{Cl} \cdot \text{H}_2\text{O}$. The oxidation state of rhodium in the rhodium(II) complex was found to be +2 by the oxidation-reduction reaction. These ions prefer to have octahedral geometry.

The i.r. spectrum of Ru(III) complex is similar to that of Pt(IV) complex, except those differences in the spectrum arising due to large charge on the platinum(IV). This indicates the ligand to behave as tridentate.

The spectrum (band position-wise) of Rh(II) complex is again very similar to cobalt(II) complex, $\text{Co}(\text{TH}_2)_2 \cdot 6\text{H}_2\text{O}$ (Chapter V) in which case the ligand behaved as bidentate.

These complexes are diamagnetic. This suggests that the magnetic moment due to one unpaired spin in both the complexes has been quenched forming metal to metal bond, which can be either σ -type or δ -type of bond. The quenching of magnetic moment can also take place through superexchange mechanism also. However, it will be difficult to decide among the three possible ways through which the quenching can take place.

The visible spectra of these complexes showed a very broad band (half width = 150 m μ) with a maxima of around 14,300 cm^{-1} . It is very difficult to assign this band to any particular transition and no useful information can be derived out of it.

Thus on the basis of the i.r. and the magnetic moments of these complexes along with structure of the previous diamagnetic complexes of these ions,¹⁷⁻¹⁹ the tentative structure XII and XIII may be proposed for these complexes.

Table I

Assignments of the Major Infrared Bands of the Ligand, Sodium Salt of the Ligand and the Complexes (cm^{-1})

Ligand	Sodium salt of the ligand	Complexes	Assignments
-	-	3400 ^a (B)	$\nu(\text{OH})$
3130	-	$\sim 3140 \pm (10)$	$\nu(\text{N-H})$
2400	-	$\sim 2400^b(\text{W.B})$	$\nu(\text{S-H})$
-	-	1620 ^a	(O-H) in plane bending mode
1520(B) (splitted)	1490	$\sim 1500(\text{B}) \pm (10)$ (splitted)	Thioamide band I ^c $+\nu(\text{C=C}) + \nu(\text{N=N})$
1455(W)	1455(W)	$1455(\text{W}) \pm (10)$	$\nu(\text{N=N}) + \nu(\text{C=C})$
-	1160 1100	1170^d $1110) \pm (10)$	$\nu(\text{C-N})$
1060	1015	1090	Thioamide band III ^e
940 (splitted)	860 (splitted)	860^f (splitted)	$\nu(\text{C-S})^g$
-	-	880 ^a	$\delta(\text{O-H})$
815	800	~ 845	Thioamide band IV ^h
-	-	~ 350	$\nu(\text{M-S})^i$

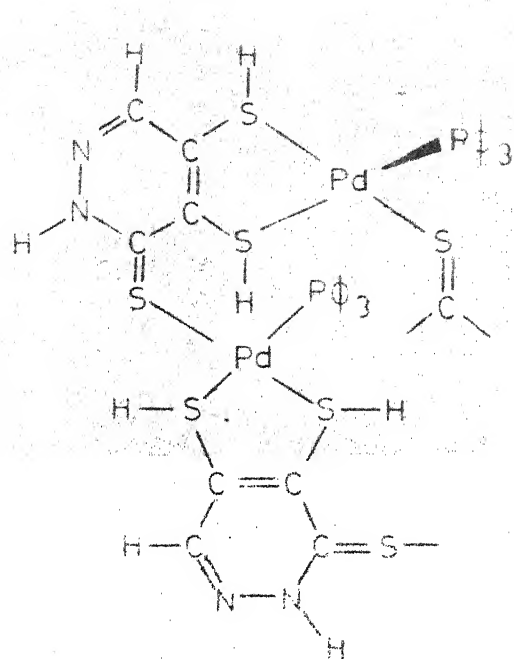
a) Present in Ru(III), Ru(II) and Rh(II) complexes; b) Present in all complexes except those of Ru(III) and Pt(IV); c) Due to $\delta(\text{N-H}) + \nu(\text{C-N})$; d) The intensities of these bands are relatively higher in Pt(IV) and Ru(III) complexes; e) Mainly due to $\nu(\text{C-N}) + \nu(\text{C=S})$; f) In case of Pd(0) and Rh(I), the band position shifts to 790 cm^{-1} and 810 cm^{-1} respectively; g) Characteristic band ω_2 of cis-dithiol group $+\nu(\text{C=S})$ of thioamide group; h) Mainly due to $\nu(\text{C=S})$; i) The positions of these bands varies with the metal ion.

Table II

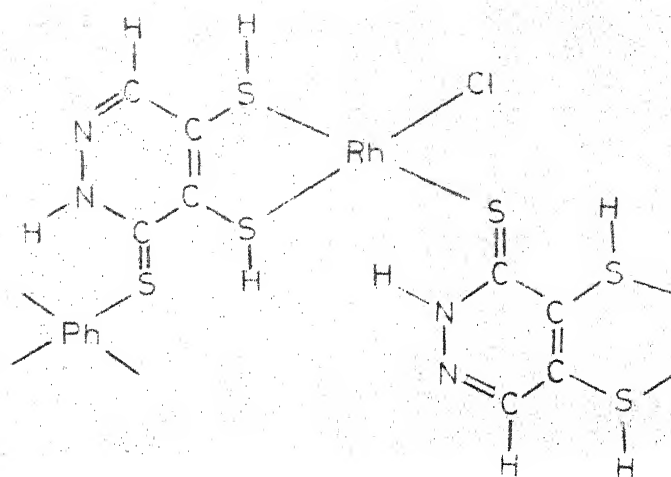
Solubilities and the Magnetic Moments of the Complexes

Complexes	$\mu_{\text{eff.}}$ B.M.	Solubility
(a) Mono(3,4,5-pyridazine trithiol)mone-(triphenylphosphine)palladium(0). $\text{Pd}(\text{TH}_3)\text{P}\phi_3$	D	I
(b) Tris(3,4,5-pyridazine trithiol)-dipalladium(II). $\text{Pd}_2(\text{TH})_2(\text{TH}_3)$	D	I
(c) Tris(3,4,5-pyridazine trithiol)-monochloro-rhodium(I). $\text{Rh}(\text{TH}_3)_3\text{Cl}$	D	I
(d) Tetrakis(3,4,5-pyridazine trithiol)-diaquo-dirhodium(II). $[\text{Rh}(\text{TH}_2)_2\text{H}_2\text{O}]_2$	D	I
(e) Tris(3,4,5-pyridazine trithiol)-dirhodium(III). $\text{Rh}_2(\text{TH})_3$	D	I
(f) Tris(3,4,5-pyridazine trithiol)-hexaaquo-diruthenium(II). $\text{Ru}(\text{TH})(\text{TH}_2)_2 \cdot 6\text{H}_2\text{O}$	D	I
(g) Mono(3,4,5-pyridazine trithiol)mono-chloro-monoquo-ruthenium(III). $\text{Ru}(\text{TH})\text{Cl} \cdot \text{H}_2\text{O}$	D	I
(h) Tris(3,4,5-pyridazine trithiol)-diplatinum(II). $\text{Pt}_2(\text{TH})_2(\text{TH}_3)$	D	I
(i) Bis(3,4,5-pyridazine trithiol)-platinum(IV). $\text{Pt}(\text{TH})_2$	D	I

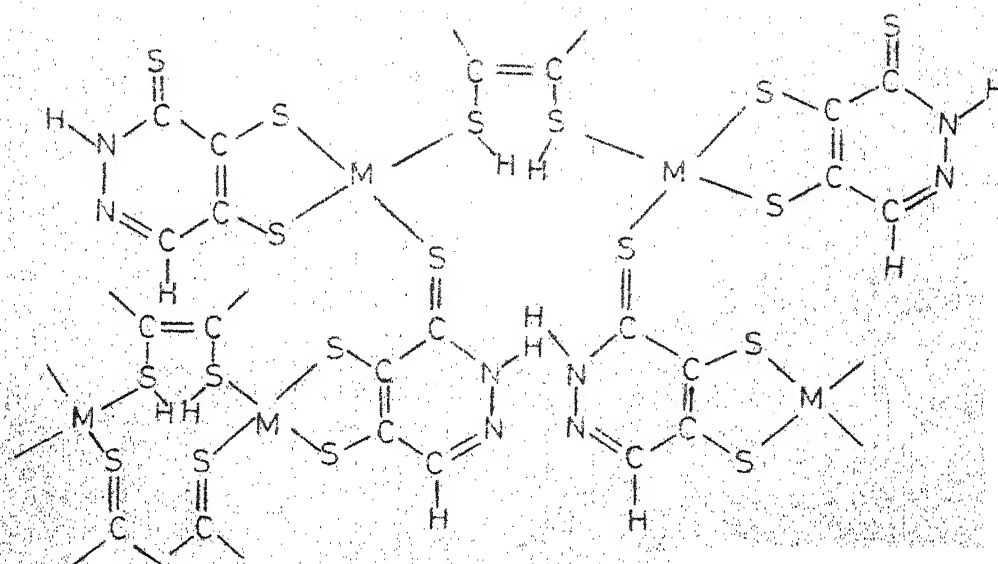
D) Diamagnetic; I) Insoluble in chloroform, carbontetrachloride, benzene, tetrahydrofurane, cyclohexane, xylene, toluene, acetone, methanol, dioxane, dichloro-ethane and dichloro-methane.



Pd (o)
(VI)

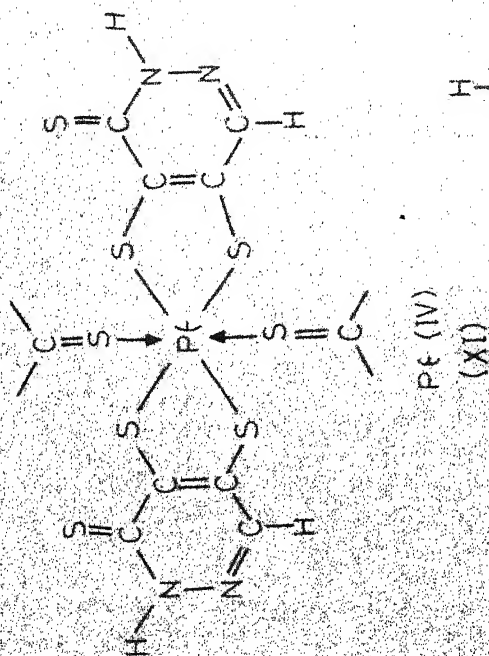
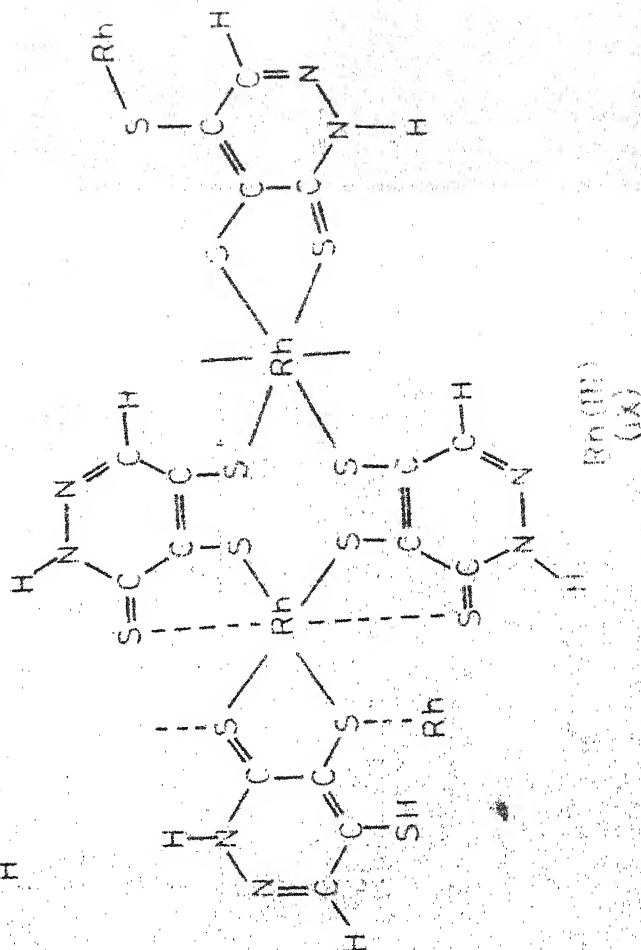
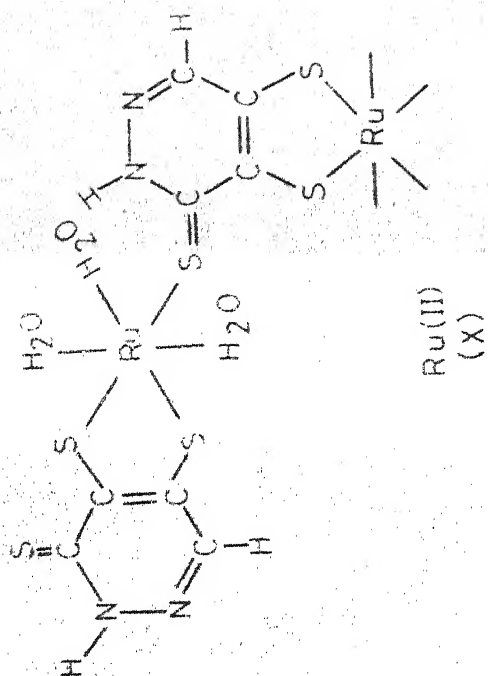


Rh (I)
(VII)



M = Pt (II) Or Pd (II)

(VIII)



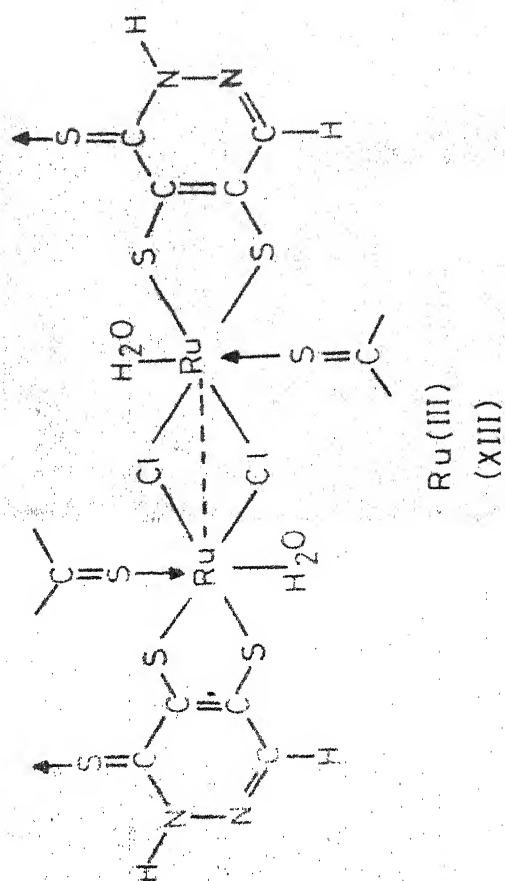
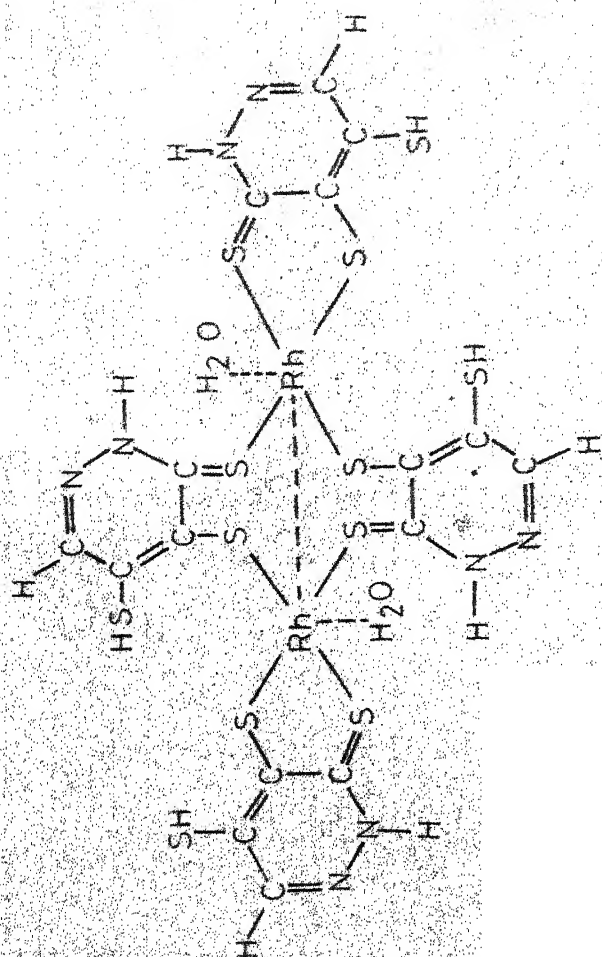


Fig. VI.1

1. 3,4,5-Pyridazine trithiol
2. Sodium salt of 3,4,5-Pyridazine trithiol
3. $\text{Pd}(\text{TH}_3)\text{PO}_3$
4. $\text{Pd}_2(\text{TH})_2(\text{TH}_3)$
5. $\text{Rh}(\text{TH}_3)_3\text{Cl}$
6. $[\text{Rh}(\text{TH}_2)_2\text{H}_2\text{O}]_2$
7. $\text{Rh}(\text{TH})_3$
8. $\text{Ru}(\text{TH})(\text{TH}_2)_2 \cdot 6\text{H}_2\text{O}$
9. $\text{Ru}(\text{TH})\text{Cl} \cdot \text{H}_2\text{O}$
10. $\text{Pt}_2(\text{TH})_2(\text{TH}_3)$
11. $\text{Pt}(\text{TH})_2$

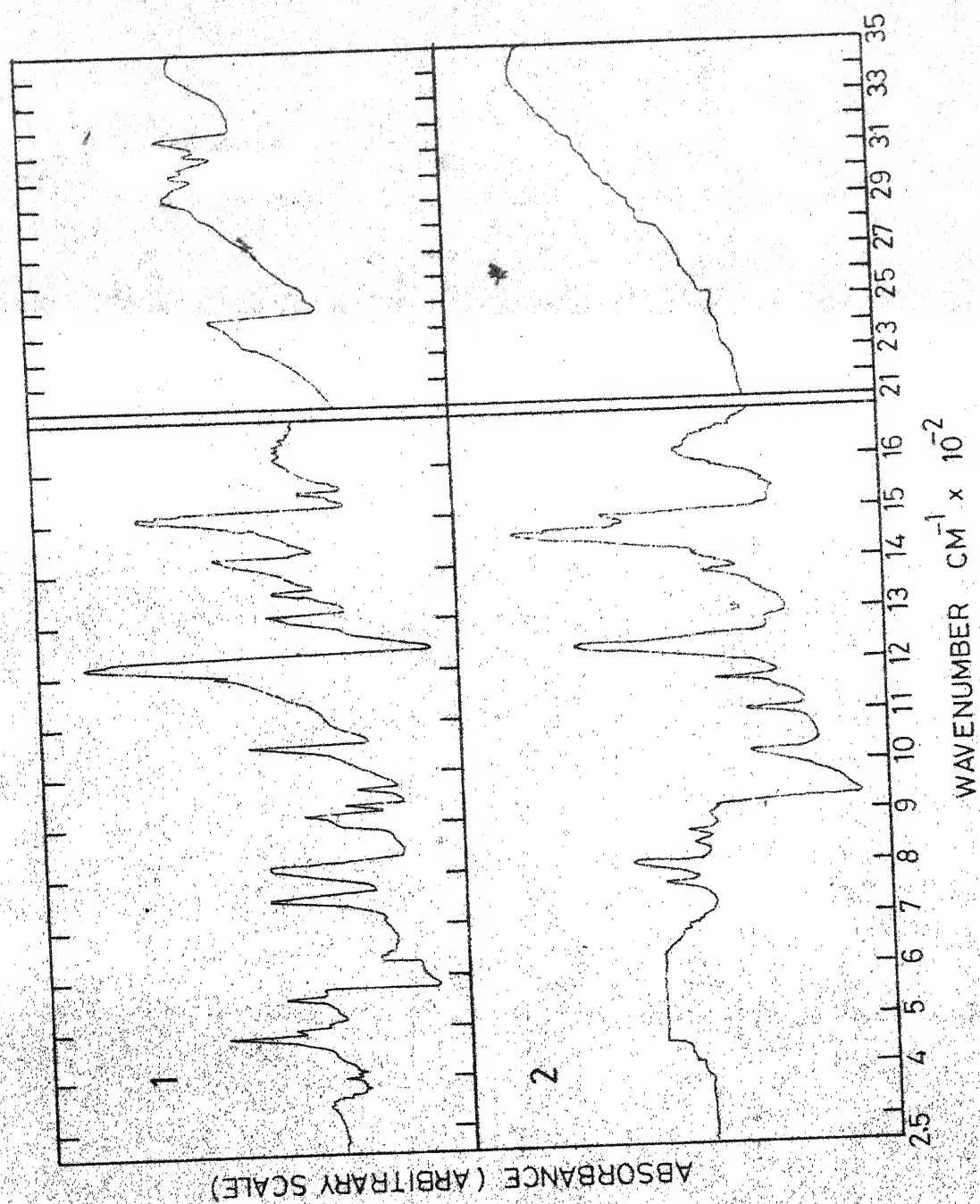


Fig. VI.1

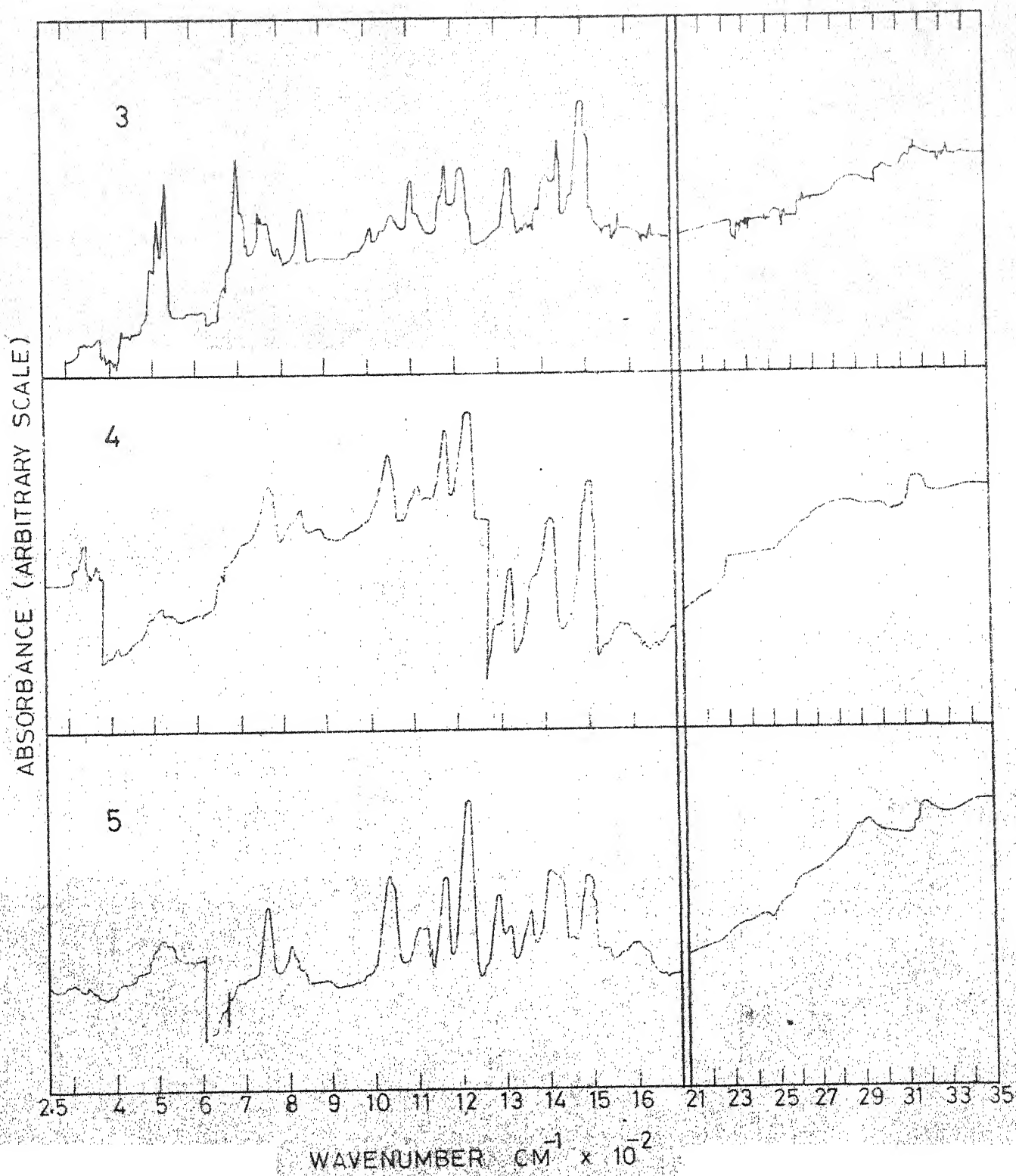


Fig. VI.1

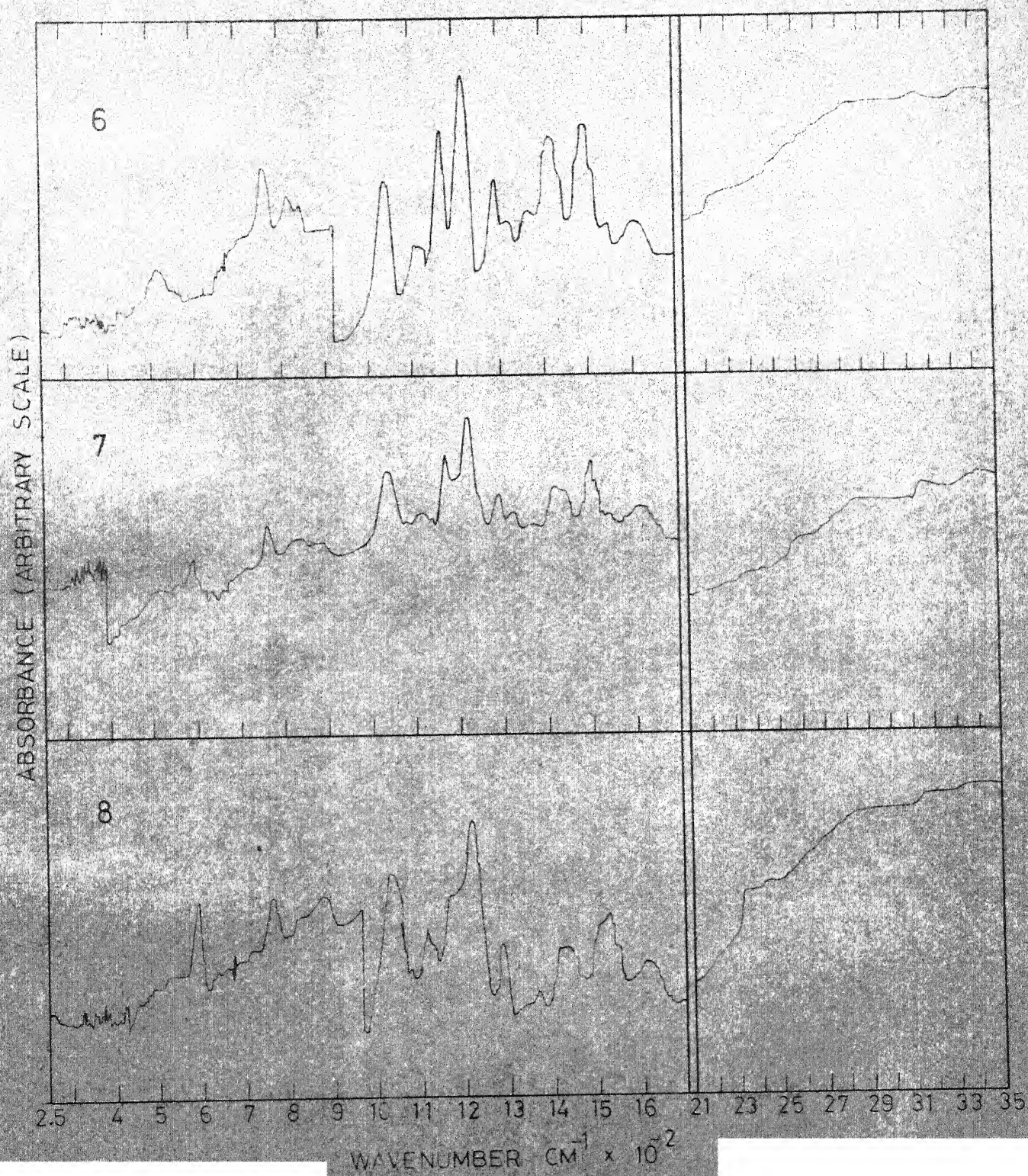


Fig. VI.1

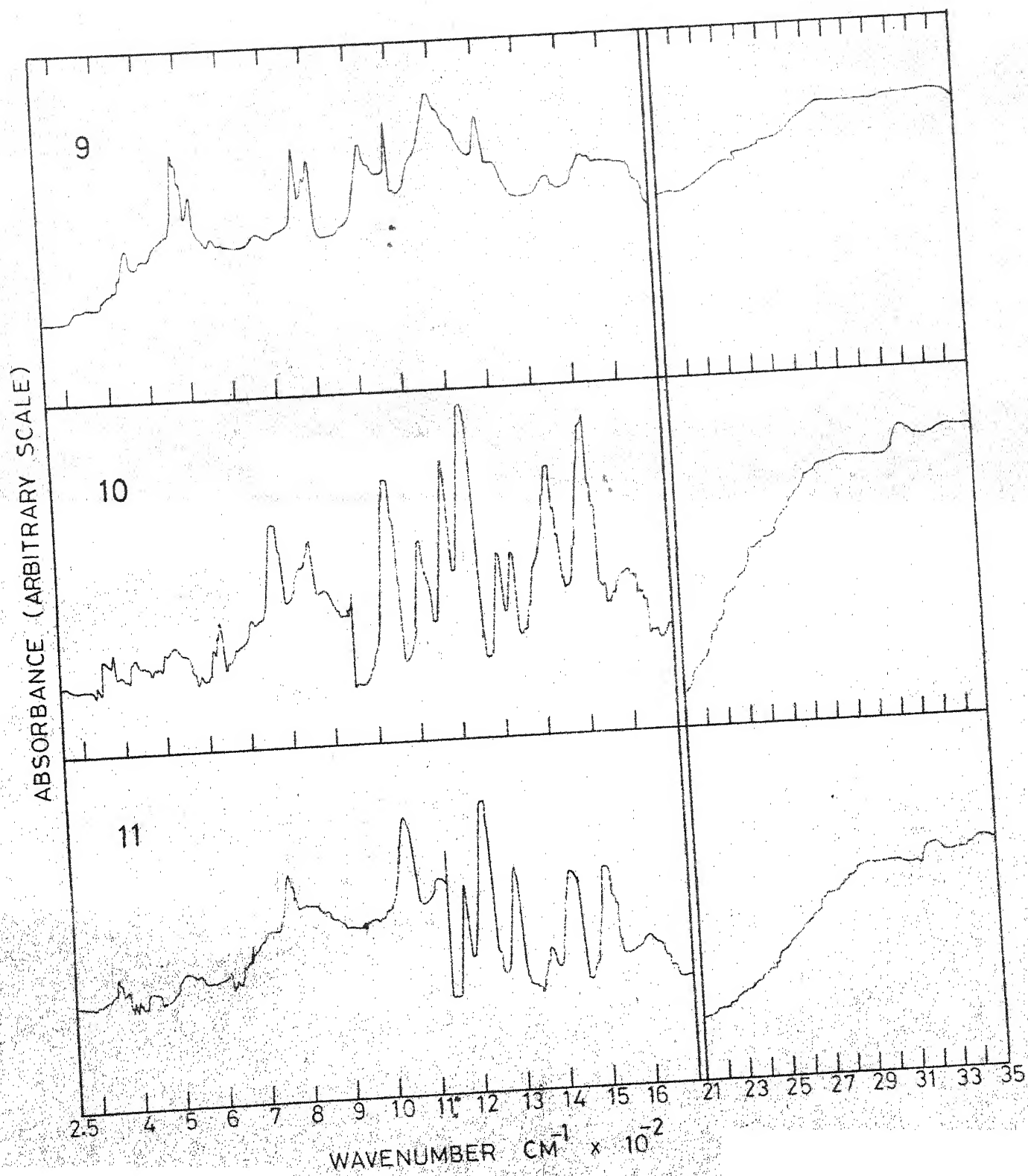


Fig. VI.1

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CHAPTER VII

CHELATING BEHAVIOUR OF 3,4,5-PYRIDAZINE TRITHIOL-III*
(Au(III), Pb(II), Cd(II), Ag(I), Tl(I) and Hg(II))

In this chapter the preparations of the complexes with gold(III), lead(II), cadmium(II), silver(I), thallium(I) and mercury(II) with 3,4,5-pyridazine trithiol are discussed. The infrared, and visible spectra, and the magnetic moments of the complexes have been examined in detail. Based on these studies, structures of complexes have been proposed.

EXPERIMENTAL

(A) Preparation of the 3,4,5-Pyridazine Trithiol

3,4,5-Pyridazine trithiol, $C_4H_4N_2S_3$ (hereafter referred as TH_3) was prepared by the method given in Chapter V.

* Communicated to J. Inorg. Nucl. Chem. (1972).

(B) Preparation of Metal Complexes

(a) Bis(3,4,5-pyridazine trithiol)digold(III).— 0.3 g of the ligand (TH_3) (~ 1.7 mmole) was dissolved in 60 ml of ethanol and 0.2 g of AuCl_3 (~ 0.6 mmole) in 20 ml of distilled water. The two solutions were mixed, whereby a black coloured precipitate appeared. It was digested for about ten minutes on a water bath. The precipitate of the complex was centrifuged and washed successively with hot water, ethanol and finally, with ether. It was dried in an air oven at 120°C for about four hours, yielding a blackish brown coloured complex.

Anal. Calcd. for $\text{Au}_2(\text{TH})_3$: C, 15.7; H, 0.6; N, 9.2; S, 31.4; Au, 43.0. Found: C, 16.0; H, 1.0; N, 9.0; S, 31.3; Au, 43.2.

(b) Mono(3,4,5-pyridazine trithiol)cadmium(II).— 0.3 g of the ligand (TH_3) (~ 1.7 mmole) and 0.3 g of CdCl_2 (~ 1.6 mmole) were dissolved in 60 ml and 100 ml respectively of ethanol. The two solutions were mixed, whereby a yellow coloured precipitate appeared. It was digested for about four hours on a water bath. It was filtered out and washed successively with hot water and ethanol. It was dried in an air oven at 120°C , yielding a yellow coloured complex.

Anal. Calcd. $\text{Cd}(\text{TH})$: C, 16.8; H, 0.7; N, 9.8; S, 33.5; Cd, 39.2. Found: C, 17.0; H, 0.6; N, 9.6; S, 33.7; Cd, 38.9.

(c) Bis(3,4,5-pyridazine trithiol)tri-lead(II).— 0.4 g (~ 2.2 mmole) sample of the ligand (TH_3) was dissolved in 80 ml of ethanol and 1.1 g (~ 2.8 mmole) of $(\text{CH}_3\text{COO})_2\text{Pb} \cdot 3\text{H}_2\text{O}$ in 150 ml of methanol. The two

solutions were mixed, whereupon a red coloured precipitate appeared. It was digested for about three hours on a water bath. The precipitated complex was filtered out and washed successively with hot water, ethanol and methanol. It was dried in an air oven at 120°C, yielding a red coloured complex.

Anal. Calcd. for $\text{Pb}_3(\text{T})_2$: C, 9.9; H, 0.2; N, 5.8; S, 19.8; Pb, 64.2. Found: C, 10.1; H, 0.4; N, 5.7; S, 20.1; Pb, 64.4.

(d) Mono(3,4,5-pyridazine trithiol)tri-silver(I).— 0.3 g of the ligand (TH_3) (~ 1.7 mmole) was dissolved in 60 ml of ethanol and 0.9 g of AgNO_3 (~ 0.5 mmole) in 50 ml of the distilled water. The two solutions were mixed, whereby a yellow coloured precipitate appeared. It was digested for about two hours on a water bath. The precipitate of the complex was washed successively with hot water and ethanol. It was dried in an air oven at 120°C for three hours, yielding a brownish yellow coloured complex.

Anal. Calcd. for $\text{Ag}_3(\text{T})$: C, 9.6; H, 0.2; N, 5.6; S, 19.3; Ag, 65.2. Found: C, 9.8; H, 0.5; N, 5.4; S, 19.4; Ag, 65.4.

(e) Bis(3,4,5-pyridazine trithiol)tetraaquo-trithallium(I).— 0.4 g of the ligand (TH_3) (~ 2.2 mmole) was dissolved in 90 ml of ethanol and 0.6 g of the TlNO_3 (~ 2.2 mmole) in 50 ml of water. The two solutions were mixed, whereby a red coloured precipitate appeared. It was digested for about two hours on a water bath. The precipitate of the complex was filtered out and washed successively with hot water

and ethanol. It was dried in an air oven at 120°C for a few hours, yielding a dark brown coloured complex.

Anal. Calcd. for $\text{Ti}_3(\text{TH})(\text{TH}_2) \cdot 4\text{H}_2\text{O}$; C, 9.3; H, 1.2; N, 5.4; S, 18.6; Ti, 59.2. Found: C, 9.4; H, 1.5; N, 5.3; S, 18.4; Ti, 59.5.

(f) Tris(3,4,5-pyridazine trithiol)dimercury(II).— 0.6 g of the ligand (TH_3) (~ 3.2 mmole) was dissolved in 120 ml of ethanol and 0.4 g of HgCl_2 (~ 1.4 mmole) in 50 ml of water. The two solutions were mixed, whereby a yellow coloured precipitate appeared. It was digested for about two hours on a water bath. The precipitated complex was filtered out and washed successively with hot water and ethanol. It was dried in an air oven at 120°C , yielding an yellow coloured complex.

Anal. Calcd. for $\text{Hg}_2(\text{TH})_3$; S, 31.2; Hg, 43.4. Found: S, 31.5; Hg, 43.7.

Methods and Techniques

The analyses of the metal ions and sulphur were carried out by the standard methods given in the literature.^{1,2} Carbon, hydrogen and nitrogen analyses were performed by the Microanalytical Section of the Indian Institute of Technology, Kanpur, India. The analytical results are given in the text. The infrared spectra and magnetic susceptibility measurements of the complexes and the ligand (TH_3) have been carried out by the same method as given in Chapter V of this thesis. The major bands of the infrared spectra and their

assignments are given in Table I. The results of the magnetic moments of the complexes and their solubilities in the solvent are given in Table II.

RESULTS AND DISCUSSION

The analytical data (given in the text) of these complexes show that the ligand in these complexes behaves as singly, double and/or triply negatively charged anions.

The complex of silver(I) has the formula $\text{Ag}_3(\text{T})^{-3}$, in which the ligand molecule is completely deprotonated. Since the most stable Ag^{+1} complexes have linear structure³ and due to complete insolubility in all the solvents, the complex should be polynuclear. Based on these assumptions the structure (I) is proposed in which the silver is bicoordinated and the geometry around the tricoordinated sulphur is pyramidal. The i.r. spectra of the complex will be similar to the one of the sodium salt except that the shifts in the positions of the bands in the spectrum of silver complex will be much larger due to higher polarization of sulphur by silver and larger coordination. Besides due to highly polymeric nature of the complex the bands are expected to be broad ones. Exactly the same results were obtained from the i.r. spectrum of the complex. In trisodium salt, one expects bonding through sulphur atoms, similarly in silver(I) complex also, the bonding of silver atoms with sulphur atoms is postulated. Moreover, $\text{Ag}(\text{I})$ is a 'b' class⁴ metal ion, and therefore, it will link with sulphur in preference to nitrogen atom.

The formula of cadmium(II) complex is $\text{Cd}(\text{TH})$. Since cadmium in its complexes prefers to attain tetrahedral geometry³ and if this geometry is assumed in the complex, the ligand will behave as tetradentate.

The i.r. spectrum of the complex shows the following major changes as compared to that of the ligand. (a) The positions of $\delta(\text{N-H})$ and thioamide bands (I) and (II) which contains large contribution from $\delta(\text{N-H})$ have been shifted to lower wave numbers. (b) The positions of thioamide bands (III) and (IV) having major contribution from $\nu(\text{C=S})$ and $\nu(\text{C-N})$ shifted to higher wave numbers, and (c) $\nu(\text{S-H})$ bands were absent in the spectra. The direction of the shifts in the band position indicate that the bonding is through thiol sulphur after deprotonation and through thione sulphur atom and the nitrogen atom without deprotonation.

The complex is diamagnetic and the spectrum in the visible and u.v. region resembles that of the ligand with a minor shifts in the band positions. Thus, along with the i.r. spectral and analytical data indicate the structure (II) for the complex.

Lead(II) complex has the formula $\text{Pb}_3(\text{T})_2$. The i.r. spectrum is similar to that of the silver(I) complex, except that the positions of thioamide bands (III) and (IV) shifted to higher wave numbers, indicating the bonding through nitrogen. Similarly the position of $\nu(\text{C-N})$ (1160 cm^{-1}) band moves-up indicating the bonding through nitrogen atom.⁵ There is no band due to $\nu(\text{N-H})$ and $\nu(\text{S-H})$, indicating

the complete deprotonation of the ligand except >C-H group.

Assuming the preferred geometry of the lead complexes as tetrahedral,³ the structure III of the complex is proposed. This has been further substantiated by its diamagnetic behaviour.

Gold(III) complex has the formula $\text{Au}_2(\text{TH})_3$. Most of the diamagnetic four coordinated gold(III) complexes are square planar.³ The diamagnetism of the complex indicates its square planarity. Its i.r. spectrum is similar to that of cadmium(II) complex, indicating the bonding through thiol sulphur atoms after deprotonation and nitrogen atom without deprotonation. It is highly polymeric, which is suggested by the broad i.r. bands appearing in the spectrum and its complete insolubility in all the solvents. Therefore, the structure IV is proposed for the complex.

The i.r. spectrum of mercury(II) complex, $\text{Hg}_2(\text{TH})_3$, is similar to that of gold(III) complex. It is diamagnetic. Since most of Hg(II) complexes are tetrahedral,³ its geometry is assumed to be tetrahedron. Hence the structure is proposed for the complex which is similar to gold(III) complex except that around gold, the ligands are arranged in a square planar way whereas in mercury, the arrangement is tetrahedral.

The general formula for thallium(I) complex is $\text{Tl}_3(\text{TH})(\text{TH}_2) \cdot 4\text{H}_2\text{O}$. The i.r. spectrum does not show any band due to D(N-H) , but the band due to D(S-H) is present at 2400 cm^{-1} . The positions of thioamide bands I and II shifts to lower wave numbers, while those of thioamide

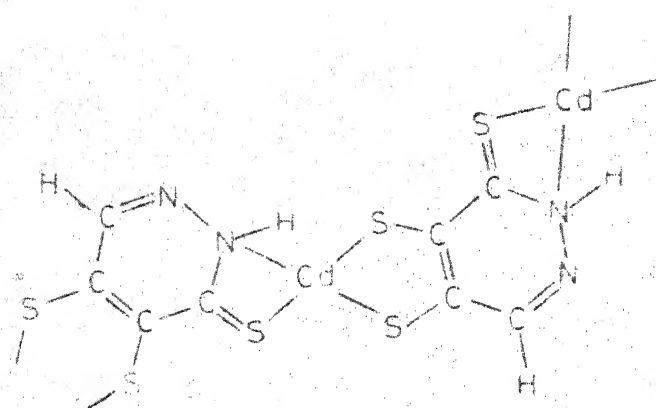
band (III) and (IV) remains practically unchanged. This indicates that H-N-C-S group is taking part in the bond formation. The bands due to $\nu(\text{O-H})$, $\delta(\text{O-H})$ and $\tau(\text{O-H})$ are present in the usual positions. (3400 cm^{-1} , 1600 cm^{-1} and 800 cm^{-1} respectively). The positions of dithiolene bands I and II at 950 cm^{-1} and 1300 cm^{-1} , shift only slightly towards lower wave numbers, indicating an interaction of thiol sulphur with metal ion. Thus, structure V is proposed for the complex.

Table II

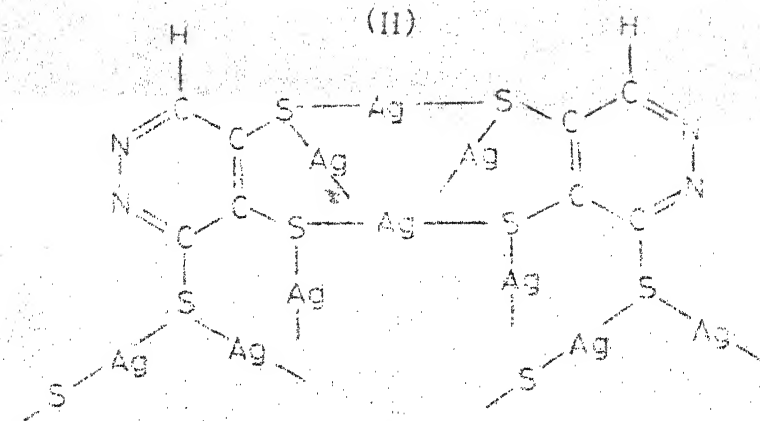
Solubilities and Magnetic Moments of the Complexes

Complexes	$\mu_{\text{eff.}}$ B.M.	Solubility
(a) Tris(3,4,5-pyridazine trithiol)- digold(III). $\text{Au}_2(\text{TH})_3$	D	I
(b) Mono(3,4,5-pyridazine trithiol)- cadmium(II). $\text{Cd}(\text{TH})$	D	I
(c) Bis(3,4,5-pyridazine trithiol)- trilead(II). $\text{Pb}_3(\text{T})_2$	D	I
(d) Mono(3,4,5-pyridazine trithiol)- trisilver(I). $\text{Ag}_3(\text{T})$	D	I
(e) Bis(3,4,5-pyridazine trithiol)- tetraaquo-trithallium(I). $\text{Tl}_3(\text{TH})(\text{TH}_2) \cdot 4\text{H}_2\text{O}$	D	I
(f) Tris(3,4,5-pyridazine trithiol)- dimercury(II). $\text{Hg}_2(\text{TH})_3$	D	I

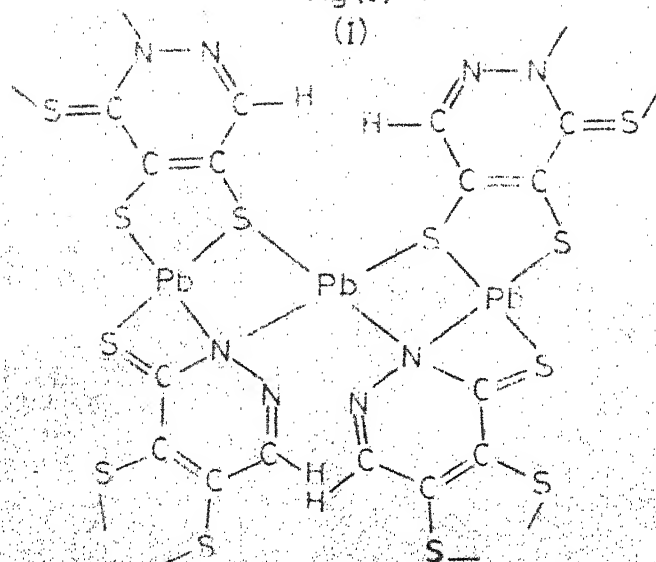
D) Diamagnetic; I) Insoluble in chloroform, carbon-tetrachloride, benzene, tetrahydrofurane, cyclohexane, xylene, toluene, acetone, methanol, dioxane, dichloro-ethane and dichloro-methane.



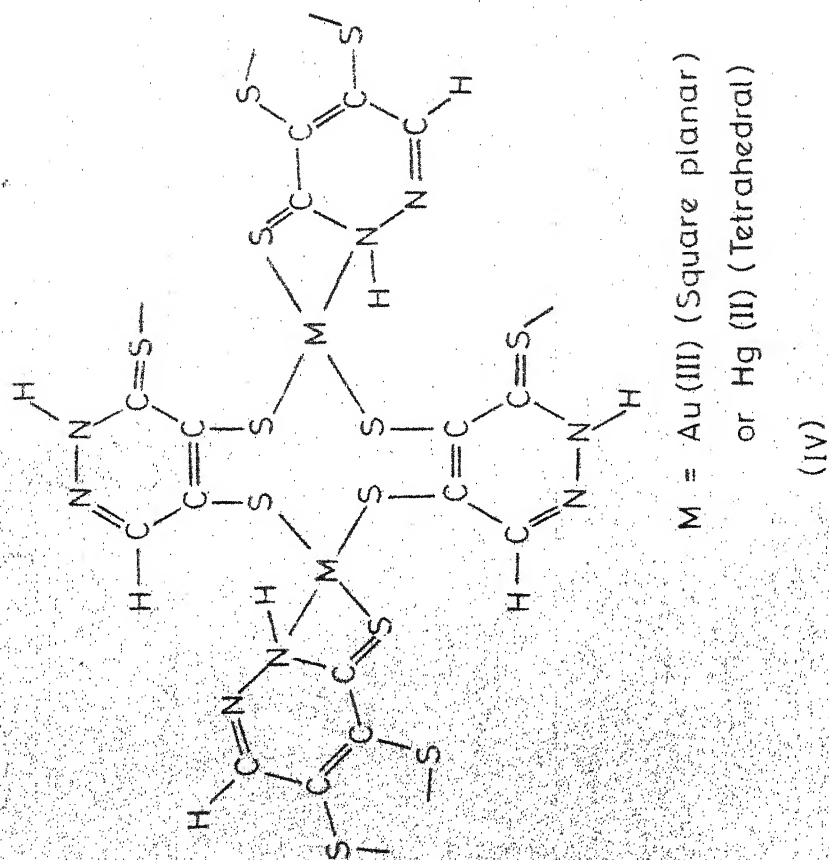
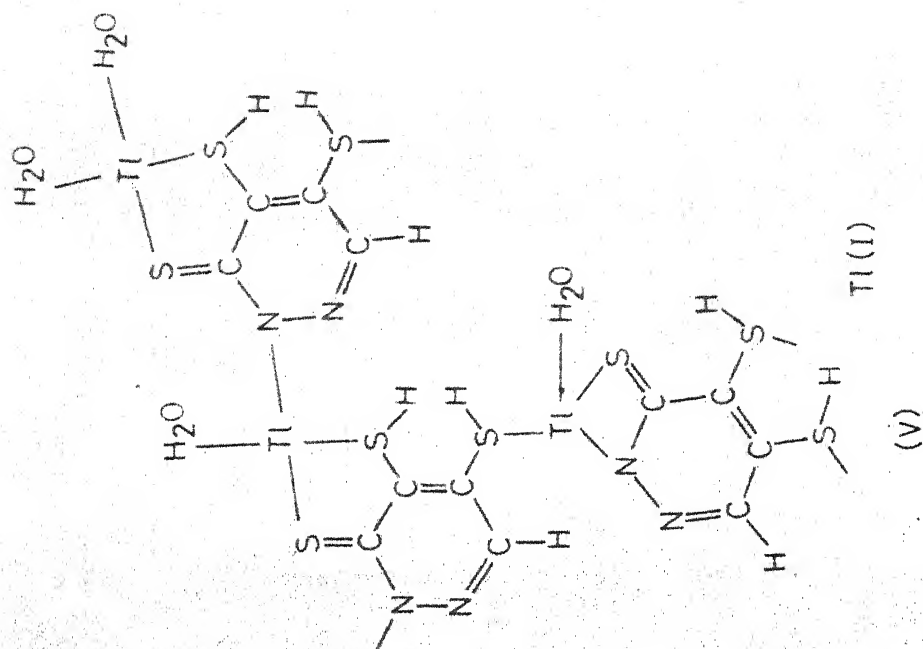
Cd(II)
(II)



Ag(I)
(I)



Pb(II)
(III)



M = Au(III) (Square planar)
or Hg(II) (Tetrahedral)

Fig. VII.1

1. 3,4,5-Pyridazine trithiol
2. Sodium salt of 3,4,5-Pyridazine trithiol
3. $\text{Au}_2(\text{TH})_3$
4. $\text{Cd}(\text{TH})$
5. $\text{Pb}_2(\text{T})_2$
6. $\text{Ag}_3(\text{T})$
7. $\text{Tl}_3(\text{TH})(\text{TH}_2) \cdot 4\text{H}_2\text{O}$
8. $\text{Hg}_2(\text{TH})_3$

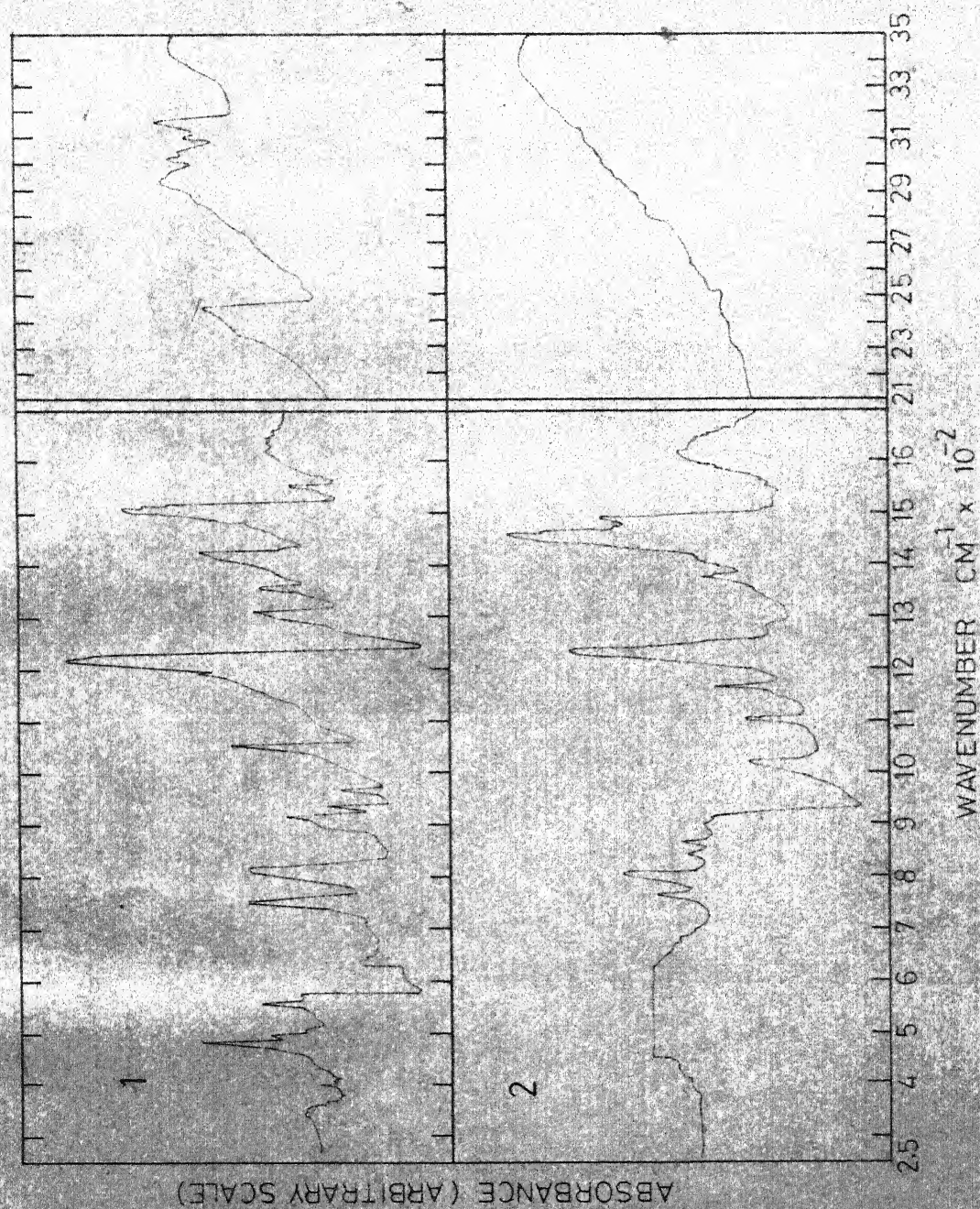


Fig. VII.1

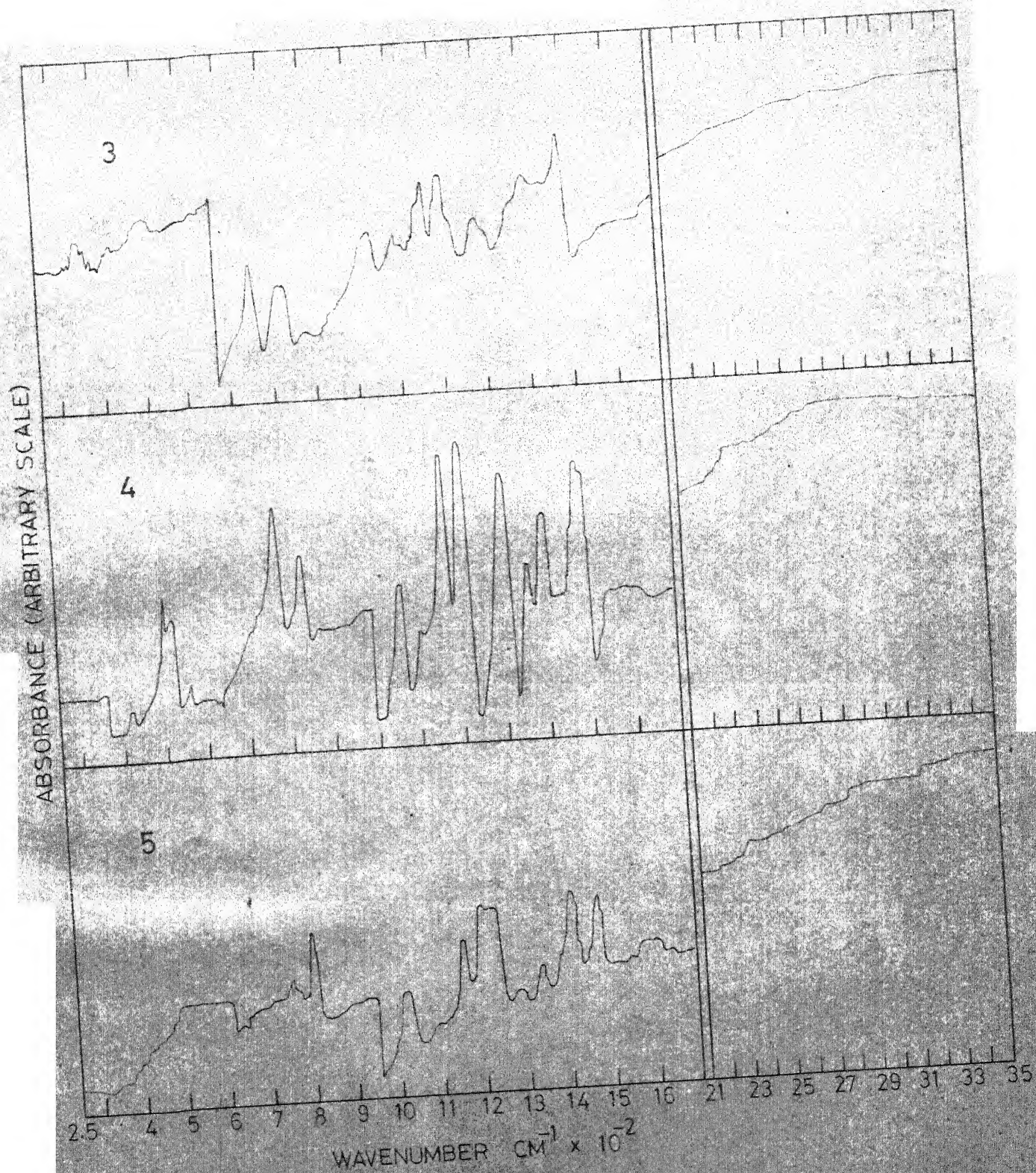


Fig. VII-1

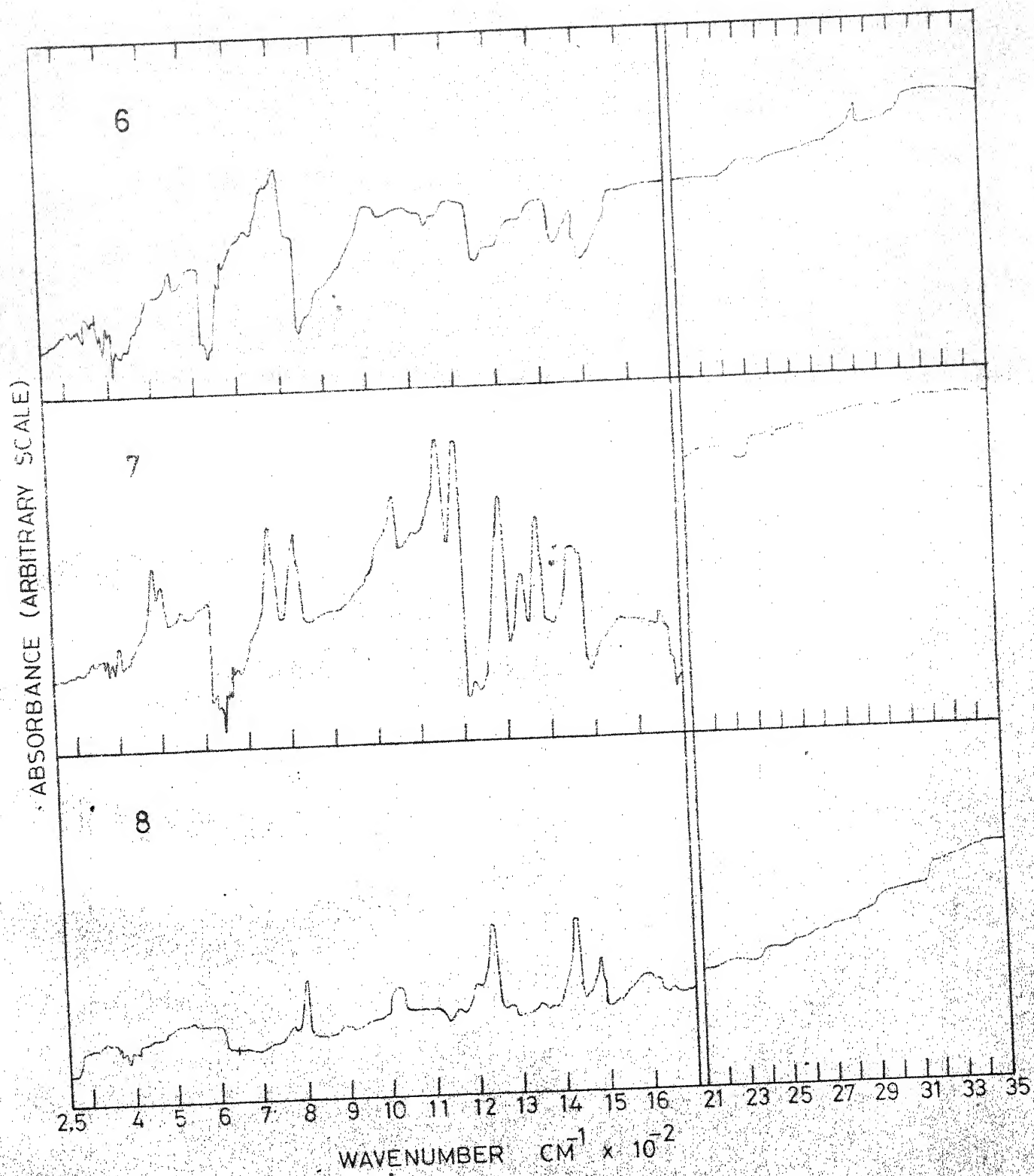


Fig. VII.1

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1. A.I. Vogel, "A Text Book of Quantitative Inorganic Chemistry", Longmans, Green and Co., London, 1962, pp. 339, 462, 482, 486, 513, 549.
2. F.P. Treadwell and W.T. Hall, "Analytical Chemistry", Vol.II, John Wiley and Sons, Inc., New York, N.Y., 1958.
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4. Ahrland J. Chatt, and N.R. Davies, Quart. Rev., 12, 265 (1958).
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CHAPTER VIII

SUMMARY

The present thesis is divided into seven chapters.

Chapter I deals with the object and scope of the work and a brief review on the complexing properties of the ligands containing H-N-C-S and HS-C=C-SH groups. In Chapter II to VII preparations of the metal complexes with 2,4-dithiouracil and 3,4,5-pyridazine-trithiol respectively and elucidations of their possible structures using analytical, spectroscopic (visible and infrared) and magnetic susceptibility data have been dealt.

The complexing behaviour of 2,4-dithiouracil(TU) has been discussed in Chapters II, III & IV. The metal ions used for complexation with (TU) were Pd(0), Pd(II), Pd(IV), Rh(I), Rh(II), Rh(III), Ru(II), Ru(III), Pt(II), Pt(IV), Au(III), Co(II), Ni(II), Cu(II), Pb(II), Cd(II), Ag(I), and Tl(I). Table I of Chapter I

describes the stoichiometries and the spatial arrangement of the ligands around the metal ions which have been arrived at using i.r., visible, spectral, and magnetic data. In some cases the numerical values of the crystal field strength of the ligand $10 Dq$, B and (B/B') have been calculated using ligand field theory and thereby the ligand's position in the spectrochemical and nephelauxetic series has been indicated. It is found that the ligand (TU) behave as tetradentate in $Cd(II)$, $Ni(II)$, $Pb(II)$ and $Ru(II)$, tridentate in $Cu(II)$, bidentate in $Co(II)$, $Tl(I)$, $Rh(III)$, $Ru(III)$, $Pd(II)$, $Pd(IV)$, $Pt(II)$, $Pt(IV)$ and $Rh(II)$, and monodentate in $Ag(I)$, $Pd(O)$ and $Rh(I)$. It has been observed that nitrogen and sulphur atoms are the bonding sites in the complexes. The complete insolubilities of all the complexes in organic and inorganic solvents predicts their polymeric nature. The structures of the complexes are given in their respective chapters.

In the next three chapters, the complexing behaviour of 3,4,5-pyridazine trithiol (TH_3) has been dealt. The metal ions used for the complexation with (TH_3) were $Pd(O)$, $Pd(II)$, $Pd(IV)$, $Rh(I)$, $Rh(II)$, $Rh(III)$, $Ru(II)$, $Ru(III)$, $Pt(II)$, $Pt(IV)$, $Au(III)$, $Co(II)$, $Ni(II)$, $Cu(II)$, $Fe(III)$, $Cr(III)$, $Pb(II)$, $Cd(II)$, $Ag(I)$, $Tl(I)$, and $Hg(II)$. The procedure for the preparations and the analytical results of the complexes are described. A brief procedure for the preparation of the ligand (TH_3) is given in Chapter V. Their i.r. spectra have been discussed. The visible spectra and the magnetic moments values

are interpreted in the light of Ligand Field Theory. The low values of the magnetic moments of the complexes Ni(II), Cu(II), Fe(III), Co(II) and Cr(III) suggest that in all these complexes there is intermetal ion interaction such that the spins of the various electrons are paired.

Due to the presence of three sulphur and two nitrogen atoms in the ligand (TH_3), it can act as mono-, bi-, tri-, tetra-, and pentadentate depending upon the mode of linkage with the metal ions. It has been found that it behaves as tetradentate in Au(III), Hg(II), Cd(II), tridentate in Ru(III) and Pt(IV), bidentate in Co(II) and Rh(II) and both bidentate and tridentate in Ru(II), Pt(II) and Pd(II). The stoichiometries and the spatial arrangements of the ligand around the central metal ions are given in Table I (Chapter I). It has been observed that the bonding in the metal complexes is through nitrogen, thiocarbonyl sulphur and dithiolene sulphur atoms. The complete insolubilities of all the complexes in organic and inorganic solvents predicts their polymeric nature. The structures of the complexes are given in their respective chapters.

The presence of the bands due to (N-H) group around 3100 cm^{-1} and due to (S-H) group around 2400 cm^{-1} in the i.r. spectra of the ligand (TH_3), suggests the ligand to be present in the thiol-thione form (structure X of Chapter I).

LIST OF PUBLICATIONS

1. "2,4-Dithiouracil As Complexing Agent-I",
J.S. Dwivedi and U. Agarwala,
Indian J. Chem., 10, 652 (1972).
2. "2,4-Dithiouracil As Complexing Agent-II",
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J. Inorg. & Nucl. Chem. (in Press) 1972.
5. "3,4,5-Pyridazine Trithiol As Complexing Agent",
J.S. Dwivedi and U. Agarwala,
Communicated to Inorg. Chem. (1972).
6. "3,4,5-Pyridazine Trithiol As Complexing Agent",
J.S. Dwivedi and U. Agarwala,
Communicated to J. Inorg. & Nucl. Chem. (1972).

VITAE

The author was born on 15th July, 1947 at Kanpur, U.P., India. He passed the High School and Intermediate examination in 1961 and 1963 respectively conducted by the U.P. Board Allahabad. After graduating in 1965 from the University of Allahabad, he continued his studies in the same University and obtained the Master of Science degree in Chemistry in 1967. He was lecturer at D.B.S. Post-graduate College (University of Kanpur) during 1967-1968. Later he joined the department of chemistry, Indian Institute of Technology, Kanpur as a Research Scholar on 8th Jan. 1968. Presently, he is continuing in the same department as a Research Assistant.